Abstracts of the Papers Published in Other Journals by the Staff Members of the Institute from July, 1969 to June, 1970

Nuclear Chemistry

A Review of the Intermediate Energy Nuclear Physics Research in Japan. T. Yanabu. *Design Study Report of the Laboratory of Elementaly Particles*, 175 (Aug. 1969), in Japanese.—Since 1967, a study group of intermediate energy nuclear physics was organized. Until now, about one hundred persons have been interested in this field of research. In 1968, a meeting was held to discuss about the present status in Japan sponsored by the Institute of Nuclear Study, University of Tokyo. Series of works on 300 MeV electron elastic and inelastic scattering by several nuclei were reported by the members of Tohoku University. New wave functions of C^{12} nucleus to interpret these experimental results was proposed by theoretical physicists of Osaka University. Other theoretical works on the problem of mu-mesic atoms, rediative capture of pie-mesons by the nucleus, were also proposed and discussed. In the fall of 1968, a second meeting of research group was held. Problems discussed in this meeting were the scattering of a few GeV protons by light nuclei, the spallation and the fragmentation of the nucleus by very high energy cosmic rays and the application of the Regge pole theory to the excited states of light nuclei. Correlations of nucleons in the nucleus were noticed in the high energy nucleon scattering, and also a wide range view of the fragmentation phenomena was proposed to interpret the origin of elements in the universe, the origin of cosmic rays relating to the high energy accelerator experiments.

Nuclear Relaxation and its Analogy in the Properties of Bulk Material. T. Yanabu. *Japan Atomic Energy Research Institute Report,* **JAERI 1184,** 131 (1969), in Japanese.—The nuclear reaction mechanism is reviewed from the standpoint of its time sequence. The similarity between the nuclear relaxation and mechanical relaxation of viscoelastic materials is noted. The response characteristics of the nucleus to the pulse action of the incident particle are discussed reffering the recent development in the field of computer experiments on the equilibrium attainment of many particle systems.

$B^{11}+\alpha \rightarrow \alpha+\alpha+Li^7$ Reaction at 28.5 MeV. N. Fujiwara. *J. Phys. Soc. Japan,* **27,** 1380 (1969).—Angular correlations between two alpha particles emitted from the reaction $B^{11}+\alpha \rightarrow \alpha+\alpha+Li^7$ are studied at the incident energy of 28.5 MeV. The kinematics of the final state were completely determined by measuring the momenta of two alpha particles detected in coincidence. The reaction cross sections are dominated by two body interactions between two alpha particles and between alpha particle and Li^7 nucleus. Interferences among two body interactions are observed at the over-

lapping of two body resonances. This is discussed to be due to the fact that three bodies interact in the final state.

Report on the Meeting of Intermediate Energy Nuclear Physics in Japan. T. Yanabu. *Genshikaku Kenkyu,* **14**, 827 (1970), in Japanese.—Third meeting for the research of intermediate energy nuclear physics was held at the Research Institute for Fundamental Physics, Kyoto University, on 19 and 20 March, 1970. Twenty participants from Tokyo University, Nagoya University, Kyoto University and Osaka University attended. Experimental works on the quasi-free electron-proton scattering by the protons in carbon nucleus and on the deuteron break up reaction by protons and alpha particles were reported by Dr. Kamae and by Dr. Takeuchi respectively. Theoretical analyses of Li^6(p. 2p) reaction and of Al^{27} (p. 2p) reaction were also presented by Dr. Saito and by Dr. Kudo respectively. The energies of incident particles are in the range from 100 MeV to 700 MeV. The usefulness of electron-nucleon and nucleon-nucleon quasi-free scattering to see the intra-nucleus orbit of nucleons were discussed. The needs to improve the present theory to include the effect of final state interaction between product particles and the effect of the off-shell scattering were also noticed.

A Mössbauer. Spectrometer with a Large Driving Force. R. Katano. *Nucl. Instr. and Meth.,* **83**, 187 (1970).—A constant-acceleration Mössbauer spectrometer using an electromechanical transducer driven by a high power dc-amplifier at a low sweep cycle of 2.2 cps has been developed. This system capable of activating a 500 g drive rod is useful to give the Doppler-shift velocity to a sample supported inside a liquid-helium cryostat. Details of mechanical assembly, driving dc-amplifier, operational circuit, and photo-transistor pulse generator are described.

Tartaric Acid Synthesis from L-Ascorbic Acid-1-^{14}C in Grape Berries. K. Saito and Z. Kasai. *Phytochem.,* **8**, 2177 (1969).—Young grape berries were exposed to $^{14}CO_2$ for 10 min under light and dark conditions, and changes of ^{14}C-assimilation products was surveyed during a short periods. In the light, radioactivity was found in tartaric acid immediately after $^{14}CO_2$-fixation, while in the dark, radioactivity was not detected in tartaric acid until 480 min after $^{14}CO_2$-fixation. D-Glucurono-γ-lactone-6-^{14}C, L-ascorbate-1-^{14}C, D-glucuronate-6-^{14}C and sucrose-U-^{14}C were fed to young grape berries, and the incorporation into tartaric acid was investigated. A considerable amount of radioactivity was incorporated into tartaric acid from D-glucurono-γ-lactone-6-^{14}C and L-ascorbic acid-1-^{14}C, and, in the case of L-ascorbic acid-1-^{14}C, 72 per cent of the total radioactivity was was found in tartaric acid. The tartaric acid synthesized was partly degraded; when sucrose-U-^{14}C was fed, uniformly labeled tartaric acid was obtained, but when D-glucurono-γ-lactone-6-^{14}C or L-ascorbic acid-1-^{14}C was used, most of radioactivity was localized in the carboxyl groups.

Analytical Chemistry

Amino Acid-Responsive Liquid Membrane Electrodes. M. Matsui and H. Freiser. *Anal. Letters,* **3**, 161 (1970).—Amino acid responsive electrodes based on the

use of their quaternary ammonium salts in a liquid membrane phase have been prepared for tryptophane, phenylalanine, leucine, methionine, valine, and glutamic acid.

Synergistic Effect in Solvent Extraction—Effect of the Chelating Ligands on the Stability of Lutetium Mixed Chelates with β-Diketones and Their Adducts with TOPO—. T. Shigematsu and T. Honjyo. *Bull. Chem. Soc. Japan,* **43**, 796 (1970).—The effect of the chelating ligands on the stability of mixed chelates of lutetium with β-diketones and the stability of their adducts with TOPO in benzene was studied by extracting lutetium with mixtures of two β-diketones, benzoylacetone (BzA) and dibenzoylmethane (DBM), and benzoylacetone and benzoyltrifluoroacetone (BFA), in the absence or in the presence of TOPO. The results are summarized as follows. (1) The extraction constants of Lu-BzA-DBM mixed chelates are almost the same as statistically calculated, while those of Lu-BzA-BFA mixed chelates are somewhat lower than the theoretical values. (2) The stability of the TOPO adducts of the mixed chelates increases in the order, $M(BzA)_2(DBM) \approx M(BzA)(DBM)_2 < M(BzA)_2(BFA) < M(BzA)(BFA)_2$, which is almost the same as that found among the extraction constants of the mixed chelates. The fluoromethyl group stabilizes the adduct more than phenyl group. (3) All the mixed chelates of lutetium β-diketonates bind one molecule of TOPO per metal chelate.

Synergistic Effect in Solvent Extraction—Effect of Oxygen and Nitrogen Containing Organic Bases on the Stability of Zinc(II) and Cobalt(II) β-Diketonate Adducts—. T. Shigematsu, T. Honjyo, M. Tabushi and M. Matsui. *Bull. Chem. Soc. Japan,* **43**, 793 (1970).—The effect of the organic Lewis bases acting as a synergist on the extraction of zinc(II) and cobalt(II) with benzoyltrifluoroacetone was studied. *n*-Hexyl alcohol, TBP, TBPO and TOPO were used as oxygen-containing bases, and quinoline, isoquinoline, lepidine, acridine and quinaldine as nitrogen-containing bases. The stability constants between metal chelates and the adduct forming materials in the organic phase were obtained by curve fitting method. The results are summarized as follows: (1) Zinc (II) and cobalt (II) chelates formed adducts including one or two molecules of the bases per metal ion. Adduct formation was carried out successively. (2) The stability of adducts with oxygen-containing organic bases increased in the order, *n*-hexyl alcohol < TBP < TBPO ≈ TOPO. This is the same order with that of the basicity of donor oxygen in the compounds. The stability of adducts with nitrogen-containing bases increased in the order, quinaldine < acridine < quinoline < lepidine < isoquinoline. In this case, however, the steric effect of the bases preferably contributed to the adduct formation. (3) The overall stability constants of the adducts are affected by the coordination number of the metal ions. Cobalt(II) adducts are more stable than zinc(II) adducts.

Selectivity in the Metal-Complex-Catalyzed Decarboxylation of Oxaloacetic Acid and a Role of Metal Ion in an Enzyme System. M. Munakata, M. Matsui, M. Tabushi and T. Shigematsu. *Bull. Chem. Soc. Japan,* **43**, 114 (1970).—The catalytic action of metal ions in the presence of various coordinating agents and a role of metal ions for the activations of an enzyme in a decarboxylation reaction were investigated. Many of the ligands studied decreased the catalytic activity of metal ions. However, α,α′-dipyridyl selectively enhanced the catalytic activities of divalent

metal ions, except Cu^{2+}. The activity of Cu^{2+} was specifically enhanced only with histidine and its derivatives. Histidine destroyed Ni^{2+} and CO^{2+} catalysis. The specific enhancement may be due to the increase in the electronegativities of the metal ions with $d\pi$(metal)-$p\pi$(ligand) back donation and to the stereo-configuration of the metal complexes. The catalytic behavior in these metal ion coordinating agent systems was different from that in the metal-enzyme systems. It was assumed that the activation of enzyme resulted from the change in the configuration of enzyme by the coordination of metal ions, and not from the catalytic action of metal ions enhanced by the coordination of enzyme. This was supported by the fact that the catalysis of compounds containing amino groups, active sites of enzyme, remarkably depended on the stereo-configuration. In the enzyme-model system, Mn^{2+} was generally preferable to Cu^{2+} and Ni^{2+}. The catalytic actions of Cu^{2+} and Ni^{2+} were lowered by the complex formation with the active sites. This may solve the question why, in enzymatic reactions, Mn^{2+} having small complex-forming ability is more selective and effective than Cu^{2+} and Ni^{2+} with large complex-forming abilities.

Spectrofluorimetric Determination of Europium and Samarium as Their 2-Naphthoyltrifluoroacetone-Trioctylphosphine Oxide Complexes. T. Shigematsu, M. Matsui and R. Wake. *Anal. Chim. Acta,* **46**, 101 (1969).—The europium and samarium complexes with 2-naphthoyltrifluoroacetone (NTFA) can be used for the spectrofluorimetric determination of the two metals. Low concentrations of NTFA are needed, and trioctylphosphine oxide is used to enhance the extraction; the optimum pH range is 5.5–6.5. The fluorescence intensity is stable under irradiation for>30 min. The detection limits are 0.1 p.p.b. Eu and 0.1 p.p.m. Sm. Few common ions interfere; iron(III) causes low results. Rare-earth ions, except samarium, in 50-fold amounts do not interfere with the determination of europium. Europium interferes with the determination of samarium, but a simultaneous determination is possible.

The Contents of Ash, Iron and Manganese in Marine Plankton. T. Fujita, T. Yamamoto, I. Yamazi and T. Shigematsu. *Nippon Kagaku Zasshi,* **90**, 680 (1969), in Japanese.—Plankton samples collected in the coastal and offshore sea areas around Japan were analyzed for total ash, iron and manganese. All the phytoplankton specimens were mixed collections, while the zooplankton samples included both monospecific and mixed ones. Biological composition of mixed samples were determined under a microscope. The determination of iron and manganese were made by spectrophotometric method.

Summary of the analytical results is as follows.

Mean values of mg./g. dry matter of washed sample

	Total Ash	Iron	Manganese
Zooplankton (Samples of individual species)	45 (57 samples from 31 species)	0.591 (55 samples from 30 species)	0.030 (31 samples from 23 species)

Zooplankton (12 mixed samples)	141	4.52	0.096
Phytoplankton (18 mixed samples)	541	11.2	0.215

A linear relationship was seen between iron and manganese contents through the species.

Fluorometric Determination of Trace Amount of Aluminum in Natural Water by Lumogallion Method; Masking of Ferric Iron with *o*-Phenanthroline. T. Shigematsu, Y. Nishikawa, K. Hiraki and N. Nagano. *Bunseki Kagaku,* **19**, 551 (1970) in Japanese.—Lumogallion was found as a superior reagent for the fluorometric determination of aluminum in sea water [*Bunseki Kagaku,* **17**, 1092 (1968)]. Up to 30 μg of F^- and 1000 μg of PO_4^{3-} are tolerable in this procedure. Interfering ions were Fe^{3+}, Cu^{2+}, Ti^{4+}, VO_3^- and Ga^{3+}; the concentration of each of these except ferric iron in sea water was negligible. Ferric iron interfered in this procedure. It was found that *o*-phenanthlorine prevented interference by up to 10 μg of ferric iron.

Sample water containing 0.003~2 μg of aluminum was treated with 2 ml of 4% hydroxylamine hydrochloride solution. After standing for 15 min., 1 ml of 1% *o*-phenanthroline solution and 0.5 ml of 0.01% lumogallion solution were added to the solution, and pH was adjusted to 5.0(CH_3COONH_4-CH_3COOH buffer). It was heated at 80°C for 20 min., and the fluorescence intensity of the solution was measured.

The method may be applied to the samples of natural water containing $\geqq 0.05$ μg of aluminum per liter.

Radiometric Determination of Perchlorate by Solvent Extraction as Ion Association Complex. T. Shigematsu, M. Matsui, T. Aoki and M. Ito. *Bunseki Kagaku,* **19**, 412 (1970), in Japanese.—The trace amount of perchlorate was extracted as an ion association complex with Zn-Phenanthroline (labelled with ^{65}Zn) into nitrobenzene. The activity of ^{65}Zn in organic phase corresponded to perchlorate. The method was more sensitive than the absorptiometric method.

Radioactive Analysis. K. Otozai, T. Watanabe, T. Shigematsu, Y. Kusaka, H. Tsuji, H. Nezu, Y. Kiso, T. Tamai, T. Hashimoto, M. Koyama, A. Hhyoshi and T. Mitsuji. *Bunseki Kagaku,* **18**, 91R (1969), in Japanese.—Reveiw.

Organic Reagents in Inorganic Fluorometry (I). Y. Nishikawa and T. Shigematsu. *Dotite News Letter,* **17**, 2 (1969), in Japanese.—Review.

Physical Chemistry

Comparison of the Fabric of a Sensitive Pleistocene Clay with Laboratory Flocculated Clay using the Scanning Electron Microscope. Neal R. O'Brien and E. Suito. *Maritime Sediments,* **5**, 58 (1969).—The fabric of a sensitive Pleistocene clay outcropping in the St. Lawrence River Valley was observed by a scanning electron

microscope. This fabric was compared to that produced in flocculated clay sedimented in distilled water in the laboratory. There is a similarity between the fabric of both samples. The random orientation and open texture is apparent in both samples. It seems likely that the fabric of the Pleistocene clay could be produced by deposition in the flocculated state. This state could be produced not only by sedimentation in marine water, but by deposition of a high clay concentration in fresh water. Under the latter conditions, the clay concentration is a major factor in promoting flocculation and hence random clay flake orientation.

Analysis of Particle Size by Specific Gravity Balance Method in which High Viscosity Liquid is used for Dispersion Medium. E. Suito, M. Arakawa, H. Mishima, S. Yano, H. Shirahase and S. Ishida. *Zairyo,* **18**, 531 (1969), in Japanese.—Measurement of particle size in the test of distribution particle sizes in powder by the sedimentation method, is often attended with difficulty by reason of coarse particles and of powder with high sedimentation velocity, therefore with high specific gravity.

In order to cope with such a drawback it has been a common practice to carry out the measurement in the optimum conditions fittest for the instrument employed for controlling sedimentation velocity with high viscosity medium. This, however, would entail a number of problems concerning the dispersion of samples.

The experiment described below shows the characteristics of the shimadzu Recording Sedimeter based on the specific gravity balance method, together with the experimental results showing the influence of high viscosity in the medium on the particle size distribution.

The Growth of Copper Selenide Crystals Produced by Solid-State Reaction. H. Morikawa. *Japanese Journal of Applied Physics,* **9**, 607 (1970).—Electron microscopic observation was carried out to investigate the growth of crystals produced by the reaction of vacuum-deposited selenium films with copper metal. Cuprous and cupric selenide crystals were found to grow in ribbon or fan shapes within the selenium films. The ribbon-shaped crystals were composed of many narrow crystals whose lattices were twisted with each other. The fan-shaped crystals grew radially from the tips of ribbon-shaped crystals. The growth of these crystals is explained by assuming that it is controlled by self-diffusion of copper atoms in the growing crystals.

The Metal-ligand Vibrations in the Infrared Spectra of Various Metal Phthalocyanines. T. Kobayashi, F. Kurokawa, N. Uyeda and E. Suito. *Spectrochimica Acta,* **26A**, 1305 (1970).—The infrared spectra of phthalocyanine and seven divalent metal derivatives have been recorded in the region 400–4000 cm^{-1}. The metal-ligand vibration and other metal dependent bands were found and the anomalies of Cu^{2+}- and Zn^{2+}-phthalocyanines were interpreted on the basis of electronic configurations of outer orbitals of the metals.

The Far Infrared Spectra of Phthalocyanine and its Metal Derivatives. T. Kobayashi. *Spectrochimica Acta,* **26A**, 1313 (1970),—The far infrared spectra (400–30 cm^{-1}) of phthalocyanine and its metal derivatives were systematically studied and

the assignments were proposed for the individual absorption bands observed. Particular attention was paid to the absorption characteristics of each metal phthalocyanine as well as the metal-ligand vibrations. The electronic configuration of the central metal ion was discussed on the basis of these metal-dependent bands in which the zinc derivative showed a special aspect in the spectra.

The Effect of the Particle Shape on the Measurement of Particle Size Distribution. E. Suito, M. Arakawa, H. Mishima, S. Yano, S. Ishida and K. Hayashida. *Zairyo,* **19**, 548 (1970), in Japanese.—For the measurement of particle size distribution the microscopic method has unequaled advantage over all other methods in that it can simultaneously determine both the particle size and the particle shape. Availing ourselves of such advantage of the microscopic method (in this experiment Shimadzu's Particle Size Frequency Analyzer for Microscope, Type SF-10 was used) we have been enabled to obtain the particle size distribution respecting both the length diameter and the mean diameter of the particles, and to obtain at the same time also the particle size distribution respecting Stokes' diameter by using the specific gravity balances, (in this experiment Shimadzu's Recording Sedimeter Type RS-11 was used). These experiments have afforded date to discuss how particle size distribution is subject to the effect given by the particle shape. Among the sample powder used in these experiments will be mentioned α-alumina, glass ball and oxide iron.

Shimadzu Particle Size Frequency Analyzer for Microscope Type SF-10. S. Yano, S. Ishida and K. Hayashida. *Shimadzu Review,* **27**, 47 (1970), in Japanese.—Compared with many other methods for particle size distribution measurements, the microscopic method has an unequalled advantage that it can simultaneously determine particle size distribution and particle shapes, and therefore is now widely used to obtain the references for particle size distribution measurements using various other principles.

Its disadvantage is that it is time-consuming and troublesome because it is necessary to determine the size of all the particles by some means.

This article refers to the newly-developed Shimadzu Particle Size Frequency Analyzer for Microscope Type SF-10, which permits simultaneous determination of particle size distribution and particle shapes with a considerable speed.

The Effects of Packing Structure of Powder on the Angle of Repose. M. Arakawa and M. Nishino. *Zairyo,* **19**, 554 (1970).—The effects of packing structure of powder on the angle of repose were studied. The results are as follows: the angle of repose increases when the powder is packed more densely, the angle of repose is small when the particles are spherical, becomes larger with an increase in irregularity of the particles' shape, and attains its largest with the needle like particles. This effect appears to be due to the entanglement of particles.

When the sample is composed of spherical particles of uniform size, the angle of repose is especially small. In order to examine this phenomena, model experiments with steel balls were used. The results show that a little irregularity or hole in the packing structure gives a great effect on the angle of repose. Moreover, it was found

that the friction force between the particles and their substratum on which the particles were heaped had great influence upon the occurrence of the irregularity in structure. The friction force between the powder bed and the material of substratum and the angle of repose of powder were measured. The results show generally an increase in the angle of repose with increasing friction force up to a certain value, after which there is a small increase of the angle of repose with increased friction force.

An experimental equation was obtained showing the relation of these values.

The Angle of Repose of Powder in Liquid. M. Nishino and M. Arakawa. *Zairyo,* **19**, 560 (1970).—The angles of repose of spherical glass powder and α-alumina were measured in various aqueous solutions in order to examine the effect of interparticle force on the angle of repose. NaCl, Na-pirophosphate, Na-polyphosphate and Na-polyacrylate were used for this purpose. The angles of repose were very small within a certain range of concentration of dispersing agents, for example, $10^{-4}\sim10^{-3}$ mol/L of Na-pirophosphate. The measurements of apparent particle size and sedimentation volume confirmed that the powder particles were dispersed in these solutions. In the solution of NaCl, the angle of repose increased slightly with increase of concentration. Abnormally high values were obtained with Na-polyacrylate.

In the state of dispersion, for example, in 10^{-3} mol/L Na-pirophosphate, the angle of repose decreased with the decrease of particle size and seemed to be constant in the range smaller than a certain particle size, increasing will the decrease of particle size in the solution of flocculating agent. In these two states, however, the angles of repose became nearly similar as the particle size increased.

According to the Verwey-Overbeek theory, the interparticle potentials were obtained by the measurements of ζ-potential. From these results it was explained that the angles of repose were very small and almost constant in the range were the repulsive force were larger than the weight of a particle and that they took another constant value where the weight of a particle were larger than the attractive force.

From Colloidal Morphology to Molecular Morphology (An Application of Electron Microscopy by a Chemist). E. Suito. *Journal of Electron Microscopy,* **18**, 341 (1969), in Japanese.—The studies on colloidal morphology by electron microscopy in the author's laboratory was reviewed historically. The shape, microstructure, crystal habit, lattice image and crystal growth was investigated on the particles of colloidal gold and the micro-crystals of metal phthalocyanine.

Recent Contributions in Applied Electron Microscopy. N. Uyeda and E. Suito. *Characterization of Ceramic Materials. The First U.S.-Japan Seminar on Basic Science of Ceramics,* 9 (1969).—A review mostly concerned with the characterization of materials by the use of the high resolution electron microscopy and the selected area electron diffraction.

Measurement of Specific Surface Area of Powder. M. Arakawa. *J. Res. Assoc. Powder Tech.,* **6**, 31 (1969), in Japanese.—Review.

Specific Surface Area by Gas Permeability Method in the Molecular Flow Region. M. Arakawa. *J. Res. Assoc. Powder Tech.*, **6**, 357 (1969), in Japanese.—Review.

Electron Microscopy on Organic Molecular Crystals.—Direct Observation of Organic Molecule— E. Suito. *Kagaku no Ryoiki*, **24**, 84 (1970), in Japanese.—The history of the observation on the shape of organic pigments and the direct observation of organic molecule, such as copper phthalocyanine, by a electron microscope in the auther's laboratory was stated.

The Superstructures of Gold Sol Particles and their Regularities. N. Uyeda. *Hyomen*, **8**, 79 (1970), in Japanese.—By the use of high resolution electron microscopy and electron diffraction, the finely dispersed particles of colloidal gold such as Faraday sol, sodium citrate sol and Weimarn sol were studied. The diffraction contrasts, moire fringes and the lattice images of (111) and (200) planes showed that the individual particles were composed of parallel and multiple twins. The analysis and the interpretation of these contrasts were explained on the basis of diffraction theory and image formation in electron microscopy.

X-ray and Electron Diffraction Procedures in the Investigation of Catalysis. N. Uyeda. *Shokubai*, **12**, 12 (1970), in Japanese.—The principle and the procedures are explained for the application to the study of catalysis, concerning the x-ray powder diffraction, the line broadening analysis, the electron microscopy, electron diffraction (HEED) and the low energy electron diffraction (LEED).

Several examples of the application are also described in regard to the practical catalytic problems.

Particle Size Measurement. M. Arakawa. *Powder and Industry*, **2**, 24 (1970), in Japanese.—Review.

Particle Size Measurement. M. Arakawa. *Color Material*, **43**, 333 (1970), in Japanese.—Review.

Measurement of Powder Characteristics(III). Particle Size Measurement. M. Arakawa. *J. Soc. Material Sci., Japan*, **19**, 612 (1970), in Japanese.—Review.

Measurement of Powder Characteristics(IV). Measurement of Specific Surface Area of Powdered Materials. M. Arakawa. *J. Soc. Material Sci. Japan*, **19**, 685 (1970), in Japanese.—Review.

Cohesion of Particles and the Properties of Powders.—Consideration in Several Model Experiments—. M. Arakawa. *J. Res. Assoc. Powder Tech.*, **7**, 209 (1970), in Japanese.—Bulkiness and packing structure of powder was discussed by the consideration based on the particle size and cohesiveness.

Four papers were reviewed in Japanese.

1) M. Arakawa, *J. Japan Soc. Powder Metall.*, **15**, 55 (1968).
2) M. Arakawa, E. Suito, *J. Soc. Material Sci. Japan*, **17**, 642 (1968).
3) M. Arakawa, *J. Soc. Material Sci. Japan*, **16**, 319 (1967).
4) M. Arakawa, M. Nishino, *J. Soc. Material Sci. Japan*, **19**, 548 (1970).

The Structure of Some Organo-Bentonite. M. Arakawa. *Journal of Clay Science Society of Japan*, **10**, 8 (1970), in Japanese.—The structure of octadecylamine-bentonite, trimethyl-octadecylamine-bentonite and steramide-octadecylamine complex bentonite were studied by various methods. The relation between the organic content and the separation of the crystal layer of montmorillonite was measured by x-ray diffraction. The adsorption state of these organic molecules on the lattice layers of montmorillonite lamellae has been studied by infrared spectra and differential thermal analysis. These results suggest that the octadecylamine-bentonite was-prepared by cation exchange adsorption as usually considered. On the other hand, from the results of DTA and infrared spectrum for the octadecylamine-steramide complex bentonite, it was concluded that the steramide and octadecylamine between the lattice layer of mont-morillonite was associated in the mole ratio of 1 : 1, and steramide molecule was chemically bonded by a hydrogen bond with crystal lattice of montmorillonite. The lattice images corresponding to (001) planes of these organic bentonite were observed by electron microscope.

Electron Microscopy on Bentonite. E. Suito and T. Yoshida. *Bentonite*, 22 (1970), in Japanese.—Recent studies of bentonite by electron microscope were reviewed. Some of montmorillonite particles in Guma bentonite has curled edges at which lattice images of layers were observed. The lattice images show defect layer structure of mono ionic montmorillonite of Na^{+}, Mg^{++} and Al^{+++}.

Characteristic of Organo-Bentonite. M. Arakawa and T. Yoshida. *Bentonite*, 35 (1970), in Japanese.—A mechanism of ion exchange reaction occuring between montomorillonite and various n-primary aliphatic amines was reviewed. The values of free energy of adsorption, differential thermal analysis and infrared spectrum show that the size of alkyl chain of the amines is a important factor on the arrangement of adsorved organic spacies between the layer of the bentonite.

Lattice images of the layer of octadecyl ammonium-montmorillonite were observed at the curled edge of the particle. Many dislocations were seen in the lattice images.

Utilization of Organo-Bentonite for Chemical Industry. M. Arakawa. *Bentonite*, 118 (1970), in Japanese.—Review.

Dielectric Relaxation and Molecular Motion in Poly (Vinylidene Fluoride). S. Yano. *J. Polym. Sci., Part A-2*, **8**, 1057 (1970).—The dielectric properties of poly (vinylidene fluoride) have been studied in the frequency range 10 Hz to 100 kHz at temperatures between −196 and 150°C. Three dielectric relaxations were observed: the α relaxation occurred near 130°C, the β near 0°C, and the γ near −30°C at 100 kHz. In the α relaxation the magnitude of loss peak and the relaxation times increased

not only with increasing lamellar thickness, but also with decrease of crystal defects in the crystalline regions. In the light of the above results, the α relaxation was attributed to the molecular motion in the crystalline regions which was related to the lamellar thickness and crystal defects in the crystalline phase. In the β relaxation, the magnitude of the loss peak increased with the amount of amorphous material. The relaxation times were independent of the crystal structure and the degree of crystallinity, but increased slightly with orientation of the molecular chains by drawing. The β relaxation was ascribed to the micro-Brownian motions of main chains in the amorphous regions. The Arrhenius plots were of the so-called WLF type, and the "freezing point" of the molecular motion was about −80°C. The Cole-Cole distribution parameter of the relaxation time α increased almost linearly with decreasing temperature in the temperature range of the experiment. The γ relaxation was attributed to local molecular motions in the amorphous regions.

Dielectric Relaxation in Copolymers of Vinylidene Fluoride and Hexafluoropropylene. N. Koizumi, K. Tsunashima, and S. Yano. *J. Polym. Sci., Part B*, **7**, 815 (1969).—Dielectric Relaxation and glass transition in copolymers of vinylidene fluoride (VDF) and hexafluoropropylene (HFP) were studied at frequencies of 10 Hz to 100 kHz over the temperature range of −195 to 100°C. The copolymers exhibited two relaxation processes, β and γ, above and below glass transition temperature, respectively. In addition to these relaxations copolymers with low HFP contents showed another relaxation associated with crystalline regions at high temperature. With increasing HFP contents the β relaxation moved to higher temperature in accordance with shift of the glass transition temperature. The HFP content was closely connected with molecular movements in copolymers. The β relaxation was attributed to the micro-Brownian motion of molecular chains in amorphous regions. The γ relaxation which was much smaller in size and slightly dependent on temperature was assigned to a local mode relaxation associated with movements of short segments of molecular chains.

Studies on Molecular Orientation by Spectropolarimetry. R. Gotoh, N. Kimura and S. Hayashi. *Kôgyô Kagaku Zasshi*, **73**, 1482 (1970), in Japanese.—It has been shown that anisotropic absorption or dichroism due to molecular orientation can be discussed in terms of optical rotation recorded with a spectropolarimeter. When a polyvinyl chloride film containing anthracene was stretched, so-called optical rotatory dispersion curves were obtained at various elongations corresponding to the absorption spectrum of anthracene.

The optical rotatory power $\alpha°$ at respective frequencies is related to the optical densities, $A_{\parallel}$ and $A_{\perp}$, parallel and perpendicular, respectively, to the direction of stretching, as follows:

$$2\log\{\tan(45°-\alpha)\} = A_{\parallel} - A_{\perp} = D\,, \qquad (1)$$

where D is the "dichroic difference".

Taking θ as an average angle between the stretching direction and the transition moment of the absorption band, the orientation function F is given by the relation,

$$F = \frac{1}{2}(3\overline{\cos^2\theta} - 1) = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \,. \qquad (2)$$

The orientation function of polyvinyl chloride was obtained by using polarized infrared spectroscopy and compared with that of anthracene at respective elongations.

Simultaneous Measurements of Stress and Infrared Dichroism on Polymers. II. Continuous Elongation and Stress Relaxation of Polychloroprene. T. Takenaka, Y. Shimura, and R. Gotoh, *Kolloid-Z. u. Z. Polymere,* **237**, 193 (1970).—In order to obtain informations on the molecular nature and mechanism of rheological processes on polymers, simultaneous measurements of stress and infrared dichroism were made of polychloroprene (Neoprene Type AC) films during the course of continuous elongation at the constant rate 25% min and of stress relaxation at 400% elongation. The time dependence of the infrared dichroism was obtained by measuring the intensity change at fixed wavenumbers of absorption band maxima of the differential polarized infrared spectra. Both the degree of crystallinity of sample films and the orientation function of transition moments were calculated from the results of the infrared dichroic measurements under the assumption of uniaxial orientation, which was confirmed to be the case by x-ray diffraction and birefringence measurements.

In the continuous elongation experiments, it was found that the orientation function for crystalline-sensitive bands showed maxima at 25% elongation and then decreased rapidly, changing their signs from positive to negative. There also appeared the yield point in the stress-strain curve and the beginning of sharp decrease of crystallinity at the same degree of elongation 25%. These facts were interpreted in terms of the orientation of the crystalline phase followed by the degradation of crystallites and drawing out of the molecular chain from the crystallites. In the stress relaxation experiments, moderate changes in the orientation functions were found for various characteristic absorption bands. Little difference was observed between changes in the orientation functions for the amorphous and crystalline-sensitive bands. This makes a contrast with the previous results for vulcanized natural rubber, where the orientation of the crystalline phase was completed almost immediately after elongation, while in the amorphous phase the molecular chains were oriented gradually during the course of stress relaxation.

Magnetic Properties of Organic Stable Radicals. II. Porphyrexide. T. Fujito, H. Nishiguchi, Y. Deguchi and J. Yamauchi. *Bull. Chem. Soc. Japan.,* **42**, 3334 (1969).—Magnetic susceptibility of an organic stable radical, porphyrexide, was measured from 1.5°K to 300°K. Magnetic susceptibility follows Curie-Weiss law (Weiss constant-8°K) from 300° to 20°K then deviates from this law, reaches a broad maximum at 7.2°K, and decreases below 7.2°K. The observed value fits the theoretical linear Ising model better than the others, (linear Heisenberg model, pari model).

Inorganic Chemistry

Growth of V_3O_5 and V_6O_{11} Single Crystals. K. Nagasawa, Y. Bando and T. Takada. *Japan. J. Appl. Phys.,* **8**, 1267 (1969).—This paper reports on preparation

of V_3O_5 and V_6O_{11} single crystals by chemical transport reaction using $TeCl_4$ as chemical transport agent. The experimental procedure is the same one for V_4O_7 and V_7O_{13} single crystal preparation. Single crystals were about 10 mm in length. The x-ray and magnetic measurement showed that the phases of single crystals were of V_3O_5 and V_6O_{11} respectively.

Growth of V_5O_9 Single Crystals. K. Nagasawa, Y. Bando and T. Takada. *Japan J. Appl. Phys.*, **9**, 407 (1970).—The authors have made efforts for growth of single crystals of intermediate vanadium oxides between VO_2 and V_2O_3 which are expressed by general formula V_nO_{2n-1}. They have obtained single crystals of V_3O_5, V_4O_7, V_6O_{11} and V_7O_{13} except V_5O_9 by chemical transport reaction using $TeCl_4$. The preparation of V_5O_9 single crystals wes difficult, because it was difficult to prepare single phase V_5O_9 powder in comparison with other vanadium oxides. This paper reports on preparation of V_5O_9 single crystals by the same method as that for VO_2, V_4O_7, *etc.*

Growth of V_4O_7 and V_7O_{13} Single Crystals. K. Nagasawa, Y. Bando and T. Takada, *Japan J. Appl. Phys.*, **8**, 1262 (1969).—This paper reports on preparation of V_4O_7 and V_7O_{13} single crystals by chemical transport reaction using tellurium tetrachloride $TeCl_4$ as a transport agent. V_4O_7 and V_7O_{13} powder were used as the starting materials and $TeCl_4$ powder of about 8.0 mg per unit volume of the silica tube was loaded into silica tube. After the tube was evacuated to 10^{-6} mmHg, it was sealed off. The sealed tube was kept heating for four days in the horizontal furnace. The single crystals obtained were bright black in color and 4~8 mm in size., From x-ray measurement and magnetic measurement, it was concluded that these single crystals were V_4O_7 and V_7O_{13}, respectively.

Electrical Properties of the V_3O_5 Single Crystals. H. Okinaka, K. Nagasawa, K. Kosuge, Y. Bando, T. Takada and S. Kachi. *J. Phys. Soc. Japan*, **27**, 1366 (1969).—Present paper treats the electrical resistivity and the thermoelectric powder α of the V_3O_5 single crystals. V_3O_5 has been clarified to be semiconducting in the temperature range from 180°K to room temperature. At 133°K, V_3O_5 has an anomaly on the temperature dependence of the magnetic susceptibility, but we could not observe the sharp anomaly on ρ *vs* T curves. The thermoelectric powder measurement shows that V_3O_5 is *n*-type semiconductor.

Electrical Properties of the V_5O_9 Single Crystals. H. Okinaka, K. Nagasawa, K. Kosuge, Y. Bando, S. Kachi and T. Takada. *J. Phys. Soc. Japan*, **28**, 803 (1970).—The V_5O_9 single crystals showed the abrupt change in electrical resistivity of the order 10^4~10^6 (ohm·cm) and metallic-to-semiconducting transition at 130°. This transition accompanies a crystallographic change like martensitic transformation.

Electrical Properties on the V_4O_7 Single Crystals. H. Okinaka, K. Nagasawa, K. Kosuge, Y. Bando, S. Kachi and T. Takada. *J. Phys. Soc. Japan*, **28**, 798 (1970.)—Present note treats the electrical resistivity and the thermoelectric powder of the V_4O_7 single crystals. Above 250°K (Tt), V_4O_7 is metallic and shows a sharp

increase in resistivity of a factor of 10^2 at Tt. Below 250°K, V_4O_7 is semiconducting with an activation energy of about 0.8 eV. The value of thermoelectric powder is $\sim 10 \sim -12$ μVl°K above Tt, and increases with decreasing temperature from 240° to 195°K. The value decreases with decreasing temperature below 195°K.

Magnetic Properties of MTa_2O_6 (M=Fe, Co or Ni). M. Takano and T. Takada. *Material Research Bulletin,* **5**, 449 (1970).—Susceptibility measurements showed that $FeTa_2O_6$, $CoTa_2O_6$ and $NiTa_2O_6$ are antiferromagnets with susceptibility maxima at 14°K, 16°K and 26°K respectively. From the detailed analysis of the Fe^{57} Mössbauer spectrum of $FeTa_2O_6$ at 4°K, the ground state orbital wave function and the direction of the magnetic moment of Fe^{2+} were determined.

Fe^{57} Mössbauer Effect and Magnetic Susceptibility of Hexavalent Iron Compounds; K_2FeO_4, $SrFeO_4$ and $BaFeO_4$. T. Shinjo, T. Ichida and T. Takada. *J. Phys. Soc. Japan,* **29**, 111 (1970).—Pure samples of three hexavalent iron compounds, K_2FeO_4, $SrFeO_4$ and $BaFeO_4$, were prepared and measurements of magnetic susceptibility and Fe^{57} Mössbauer effect were carried out down to 2°K. Those were antiferromagnetic at low temperature and the Néel temperatures of K_2FeO_4 and $BaFeO_4$ were about 5°K and 10°K respectively. The internal magnetic field extrapolated to 0°K was 140 kOe for K_2FeO_4 and 130 kOe for $BaFeO_4$. Because the Néel temperature of $SrFeO_4$ was below 2°K, the internal field was estimated from the spectrum in the presence of an external field (50 kOe). The obtained value was also about 140 kOe and the sign was found to be negative.

Temperature Shift of the Fe^{57} Mössbauer Line in the Quenched Al-0.01%Fe Alloy. S. Nasu, M. Nishio, Y. Tsuchida Y. Murakami and T. Shinjo. *J. Phys. Soc. Japan,* **27**, 1363 (1969).—The Fe^{57} Mössbauer effect in the quenched Al-0.01%Fe alloy was measured and the temperature dependence of the second order Doppler shift was observed between 4.2°K and 453°K. Analysis was carried out according to the Mannheim's expression and the force constant ratio, λ'/λ, was estimated to be 0.74.

Nucleation and Crystal Growth in Glasses. M. Tashiro. *Proceedings, Eighth International Congress on Glass 1968,* 113.—Relations between liquid-liquid, or phase separation, and crystallisation in glasses are discussed. The importance of the position of the miscibility line in the phase diagram in determining the ease of phase separation and of the subsequent crystallisation in glasses has been emphasised. The position of the miscibility line is closely related to the compatibility of oxides constituting the glasses. The ionic field strength of each cation in a glass or a combination of field strengths can be used to express the compatibility of oxides. In two-component systems, phase separation occurs on a fine scale if the two components are moderately incompatible with each other. Compatibility between the two components is markedly affected by the addition of a third component. The uniform volume crystallisation of glass is enhanced by phase separation by the following two mechanisms. Firstly the formation by phase separation of a new glassy phase whose composition is near to the future crystals; the resulting compositional match between the crystal and the

surrounding glasses with increased supercooling enhance the homogeneous nucleation of the future crystals. Secondly, concentration of special components such as TiO_2 in one of the separated phases; components so concentrated will precipitate alone or in the form of a compound, and act as heterogeneous nucleating agents. They must have critical size *i.e.* about 70Å to be effective for catalysing crystallisation.

Experimental Study on the Bending Strength of Glass in Relation to Liquid-Liquid Phase Separation. Y. Utsumi, S. Sakka and M. Tashiro. *Glass Technology*, **11**, 80 (1970).—It has been suggested that the discrepancy between the theoretical strength and the observed strength of glass may be caused partially by the inhomogeneous nature of the internal structure of glass. In order to find how inhomogeneities affect the strength of glass, the effect of phase separation on the bending strength of glass has been studied with two glasses, a lithium borosilicate glass in which spherical glassy particles were precipitated and a sodium borosilicate glass in which worm-like glassy particles were precipitated. In both the glasses the phase separation was observed uniformly in the interior of the sample, whereas it occurred only slightly at or near the original surface of the sample. The size of dispersed particles increased with time of heat treatment, but their total amount remained the same. The bending strength of the glass samples was about 15–20 kg/mm^2 before etching with hydrofluoric acid and it increased as the original surface layer was removed. This increase in strength was attributed to the removal of the flaws existing in the original surface layer. The strength measured on the glass samples which had undergone prolonged acid etching etching to remove the original surface layer varied with the time of heat treatment. This variation was attributed to the difference in size of the particles dispersed in the glasses, the strength decreasing as their size increased.

Ball Indentation Strength of Phase Separated Glasses. Y. Utsumi and S. Sakka. *Glass Technology*, **11**, 86 (1970).—The strength of glass is affected by many factors including conditions of preparation of the sample and methods of measurement. In the previous paper (Y. Utsumi *et al.*, *Glass Tech.*, **11**, 80 (1970)), results of bending strength measurements on glasses were reported. The surface layer of the glass samples was removed before measurement by etching with hydrofluoric acid to avoid the effect on the strength of the original surface caused by exposure to the ambient atmosphere during heat treatment; thus the measured strengths might have been affected by the acid etching. The ball indentation method of measuring strength was adopted in the present study in order to avoid any effects by either the original or the etched surface.

Ball indentation strengths were measured as a function of time of heat treatment for a lithium borosilicate glass and a magnesium calcium silicate glass, both of which contained spherical glassy particles as a result of metastable phase separation, and for a sodium borosilicate glass which contained worm-like glassy particles. The measurements were made on the fracture surfaces of the samples so that possible effects on the strength of the original surfaces exposed to ambient atmosphere during the heat treatment could be avoided. For all three glasses the indentation strength decreased with increasing time of heat treatment. This was attributed to the fact that the size of the particles dispersed in the glasses become larger with the time of heat treatment,

and the strength-particle size relationship was expressed approximately by the formula $\sigma = \text{const. } d^{-n}$, where n is 1/3 or 1/4.

Coloring of Alkaline Earth Sulfides Induced by Application of Shear. S. Sakka. *J. Phys. Chem.*, **73**, 2468 (1969).—Alkaline earth sulfide powders such as CaS, SrS, and BaS have been found to be sensitive in coloring behavior to the application of shear; first, these powders are weakly colored by grinding, and second, they become photosensitive. Thus, as a result of grinding and subsequent exposure to ultraviolet light, CaS, SrS, and BaS powders develop absorption bands in the visible region, peak wavelengths being at 500, 550, and 670 mμ, respectively. Possible mechanisms of coloring are discussed.

New Glasses and Recent Activities in the Field of Glass. S. Sakka. *Kagaku-Kôgyô.* **20**, 1525 (1969), in Japanese.—The recent research activities in the field of glass have been classified into (A) spectroscopic structure analysis using new methods such as IR, NMR, ESR, Mössbauer and x-ray emission, (B) study of interesting phenomena such as glass transition, electrical conduction, mixed alkali effect, metastable phase separation, crystallization and surface effects, (C) preparation of glasses using non-conventional methods such as splat cooling and vapor deposition and (D) development of new glasses. Then, the usefulness of the two-thirds-rule, $T_g/T_m = 2/3$ (T_g and T_m are glass transition and melting temperature expressed in degrees Kelvin,) in identifying non-crystalline solids as glasses have been demonstrated. Further, it has been suggested that application of the short range order concept to various interesting phenomena exhibited by solid materials may lead to discovery of new glasses. Lastly, newly developed glasses such as laser glass, switching glass, photochromic glass and self-focusing glass fiber have been cited.

Effect of Pressure on Radiation-Induced Color Centers in Silicate Glasses. T. Yamamoto, S. Sakka and M. Tashiro. *J. Non-Cryst. Solids*, **1**, 441 (1969).—Optical absorption spectra of color centers produced in silicate glasses by γ-irradiation were measured before and after application of pressure of 50 kbar to the glass. The two color center peaks, one found at about 400 nm and the other at about 600 nm, shifted toward shorter wavelengths as a result of densification of glass. The local shrinkages around the color centers estimated from the shifts of the peak wavelengths were much larger than the bulk shrinkages of the glasses obtained from the change in density of the glasses due to application of the pressure. Similar shifts of the color center peak wavelengths were observed also when the glass was γ-irradiated after densification. Besides the shift of the peaks, the application of the pressure caused a great increase of broad absorption through the visible region. A tentative explanation was given to this phenomenon on the basis of the formation of unknown defects due to the effect of shear accompanying the application of pressure. The annealing of the various pressure effects was also examined.

Effect of High Pressure on Precipitation of Silver Colloids in Glass. T. Yamamoto, S. Sakka and M. Tashiro. *Yogyo-Kyokai-Shi*, **77**, 378 (1969).—The effect of application of high pressure with an opposed-anvil type apparatus on the formation

of silver colloids in silicate glass has been studied mainly by optical absorption measurements, and the following results were obtained. 1) Application of pressure at room temperature promotes the formation of silver colloids in glass due to subsequent heating at high temperatures ranging from 250°C to 500°C. This is attributed to the effect of silver colloids by producing defect sites in glass. 2) Application of pressure at high temperatures where silver colloids form under the pressure also promotes the precipitation of silver colloids. In this case, however, the size of the particles precipitated are smaller than in the case where the glass is compressed at room temperature and subsequently heated, possibly because the application of pressure decreases the ratio of growth to nucleation rate. 3) Application of pressure to glass at room temperature after heating at high temperatures, for example, at 500°C, under atmospheric pressure has pronounced effects on the absorption spectra of silver colloids in glass: shift of absorption peaks to longer wavelengths and broadening of absorption bands. These effects are attributed to the size distribution of enlarged silver particles and/or deformed, large silver particles.

Strength of Glass-Ceramics Relative to Crystal Size. Y. Utsumi and S. Sakka. *J. Amer. Ceram. Soc.* **53**, 287 (1970).—The bending strength of a glass-ceramic produced from a crystallizable photosensitive glass has been reexamined with a special attention to the effect of the sample surface which may have a structure different from that of the bulk. The measurements conducted after the removal of the surface layer by etching with hydrofluoric acid showed that the strength increases with decreasing grain size and is expressed approximately by $\sigma \propto d^{-1/2.8}$.

Ferroelectric or Ferrimagnetic Ceramics Produced by Crystallization of glasses. T. Kokubo. *Denshi Zairyo,* **8**, (9)68 (1969), in Japanese.—Ferroelectric or ferrimagnetic ceramics produced by crystallization of glasses (glass-ceramic process) have certain advantages over the materials produced by conventional method of sintering: food formability, low sealding temperature, easy controlling of particle size, high electrical resistivity, transparency *etc.* A state-of-the-art review of the glass-ceramics containing ferroelectric crystals or ferrites is presented.

Crystallization Process of a $BaO \cdot TiO_2$-Al_2O_3-SiO_2 Glass. T. Kokubo, C. Kung and M. Tashiro. *Yogyo-Kyokai-Shi,* **77**, 367 (1969).—For the purpose of finding the cause of the preferred orientation of hexacelsian crystals near the surface of $BaO \cdot TiO_2$-Al_2O_3-SiO_2 glass-ceramics, the crystallization process of the glass with composition $BaO \cdot TiO_2$ 60, Al_2O_3 14 and SiO_2 26 mole% was investigated for at its surface as well as in the interior. Near the surface a metastable benitoite-type crystals formed firstly and then transformed progressively to the barium titanate and hexacelsian crystals whereas in the interior the latters precipitated from the first. The cause of the preferred orientation of hexacelsian crystals near the surface of the specimen was attributed to the preferred orientation of benitoite-type crystals and the resemblance of the structure between the benitoite-type crystal and hexacelsian.

Crystallization of PbO-TiO_2-Al_2O_3-SiO_2 Glasses and Dielectric Properties of their Crystallized Products. T. Kokubo, H. Nagao and M. Tashiro. *Yogyo-*

Kyokai-Shi, **77**, 293 (1969).—The glass formation region of the system PbO-TiO_2-SiO_2 is little affected by the replacement of the SiO_2 with the Al_2O_3. The glasses begin to crystallize at the temperatures 620° to 740°C and the crystals formed first are the lead titanate of the perovskite or pyrochlore type. The Al_2O_3 component promotes the precipitation of the perovskite-type $PbTiO_3$ via the glassy two-phase separation. The dielectric constant of the glass-ceramics prepared by the heat treatment at the temperatures 620° to 740°C is in the range 30 to 70 at 10^6c/s. The dielectric properties of the glass-ceramics are correlated with their microstructures, especially, the amount of the $PbTiO_3$ crystals, their axial ratio, grain size, continuity of their grains *etc.* The dielectric properties are not affected by the specimen thickness.

Thick-Film Capacitors Made from Glass-Ceramics Containing PbO and TiO_2. T. Kokubo and M. Tashiro. *Yogyo-Kyokai-Shi*, **78**, 58 (1970).—Glass powders with the compositions in the system PbO-TiO_2-SiO_2 and PbO-TiO_2-Al_2O_3-SiO_2 with or without some small amounts of other components were printed on Al_2O_3 substrates and fired up to various temperatures in the range of 600°–1000°C. A thick-film capacitor having a dielectric constant of 94 and $\tan\delta$ of 0.0130 at 10^6c/s was obtained by this method under the optimum conditions. The temperature dependence of the dielectric constant of the capacitor was almost linear in the range from room temperature to 270°C with the temperature coefficient of 0.00083/degree.

The glass powders which softened before crystallization were suitable for preparing capacitors of high dielectric constant. Otherwise, many cracks were formed in the dielectric film, which resulted in the lowering of its apparent dielectric constant.

Pressure-Induced Formation of Noble Metal Colloids in Glass. T. Yamamoto, H. Yamamoto and S. Sakka. *Physics and Chemistry of Glasses*, **11**, 11 (1970).—Many previous studies have shown that crystallization is enhanced by the application of pressure, in contrast with the theoretical prediction that pressure should retard the rate of crystal growth but so far the study of crystallization in glass has been devoted mainly to precipitation of oxide crystals, such as SiO_2 and B_2O_3, and silicates. In the present study, high pressures up to 65 kb were applied to K_2O-BaO-SiO_2 glasses containing small amounts of gold, silver, or copper ions at room temperatures where precipitation of metal colloids occurred. From the measurements of the absorption spectra due to the metal colloids precipitated at the high temperatures, it was found that the application of pressure both before heating and during heating has a pronounced effect in enhancing the precipitation of noble metal colloids. The effect of pressure is discussed on the basis of the formation of defects by pressure leading to the nucleation of colloids.

Organic Chemistry

High Pressure Synthesis of Succinic Acid from Acrylic Acid and Carbon Monoxide. N. Sugita, T. Yasutomi and Y. Takezaki. *Bull. Japan Petrol. Inst.*, **12**, 66 (1970).—Kinetic studies have been made on the synthesis of succinic acid from acrylic acid and carbon monoxide in the reaction medium of oleum as shown below:

$$CH_2{=}CHCOOH + CO \xrightarrow{H_2SO_4+SO_3} \xrightarrow{+H_2O} HOOCCH_2CH_2COOH.$$

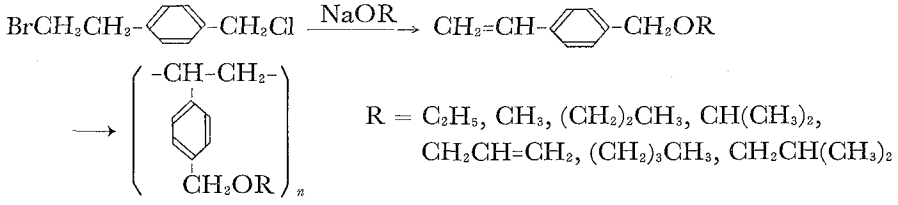
The yield of succinic acid was 75 mole % based on the charged amount of acrylic acid under the condition: temperature 40°C, CO pressure 150 atm, reaction time 8 hr, charged mole ratio acrylic acid: SO_3 : H_2SO_4=1 : 1 : 1.

Rate determinations have been carried out under such conditions that the reaction in liquid phase is rate-determining, which can be realized by reducing the concentration of the substrate with H_2SO_4.

The rate of liquid phase reaction is of the first order with respect to the pressure of carbon monoxide and to the concentration of the sultone-like complex formed from acrylic acid and SO_3, respectively.

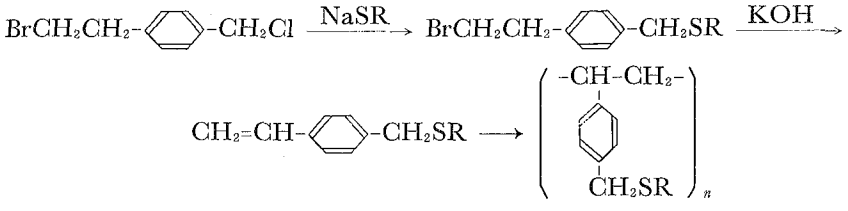
The rate constant has been found to be 8.78×10^{-4} atm^{-1} hr^{-1} at 30°C and the over-all activation energy 24 kcal $mole^{-1}$.

Syntheses of *p*-Vinylbenzyl Ethers and *p*-Vinylbenzyl Sulfides and Their Polymerizations. S. Tanimoto, M. Nishi, M. Okano and R. Oda. *Yûki Gôsei Kagaku Kyôkai Shi*, **27**, 858 (1969), in Japanese.—*p*-(*β*-Bromoethyl) benzyl chloride was treated with sodium alcoholate at room temperature to obtain *p*-vinylbenzyl ether, which could be polymerized in bulk using 2,2-'azobisisobutyronitrile as an initiator.



Sodium tert-butyrate failed to give the expected tert-butyl ether. Instead, *p*-chloromethylstyrene was the only product isolated.

Using sodium mercaptide under analogous conditions, *p*-vinylbenzyl sulfide was synthesized, from which a new polymer was obtained as follows;

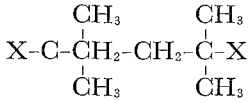


R = C_2H_5, $(CH_2)_2CH_3$

Liquid Phase Chlorination of Olefins with Cupric Chloride—Effect of Sodium Chloride Addition. S. Uemura, T. Hiramoto, Y. Takagaki and K. Ichikawa. *Kôgyô Kagaku Zasshi*, **72**, 2390 (1969), in Japanese.—Effects of sodium chloride addition on liquid phase chlorination of olefin with cupric chloride in acetic acid have been studied. Sodium chloride showed the same accelerating effect as sodium acetate (reported previously), except that considerable by-product formation was observed. Experiments have been conducted to clarify the chlorinating species

in this system. Combined with the previous results, it has been concluded that the most probable reacting species are $(CuCl \cdot OAc \cdot NaCl)_2$.

Polymeric Products from the Bi-functional Compounds Containing gem-Dimethyl Group. M. Nishi, S. Tanimoto, R. Oda and M. Okano. *Kôgyô Kagaku Zasshi*, **72**, 1941 (1969), in Japanese.—The polymeric products were synthesized by the condensation between two different kinds of the bi-functional compounds containing gem-dimethyl group. The analogous condensation were carried out between such compounds and the other proper compounds having two functional groups.



X: OH, NH_2, $NHCO_2C_2H_5$, CO_2H, COCl, CO_2CH_3, CH_2CO_2H, CH_2COCl

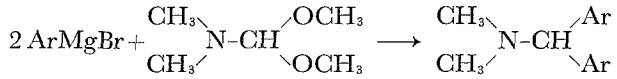
Formation and Application of Polymer *S*-Ylide. S. Tanimoto, J. Horikawa and R. Oda. *Yûki Gôsei Kagaku Kyôkai Shi*, **27**, 989 (1969), in Japanese.—*p*-Vinylphenyl methyl sulfide prepared by the reduction of *p*-(methylmercapto) acetophenone using lithium aluminium hydride with subsequent dehydration with the aid of potassium hydrogen sulfate could be bulk-polymerized in the presence of an initiator, 2,2′-azobisisobutyronitrile. The linear sulfide-type polymer so formed was treated with dimethyl sulfate to obtain a water-soluble sulfonium-type derivative. A water insoluble sulfonium-type polymer was prepared in a similar manner from a *p*-vinylphenyl methyl sulfide-divinylbenzene copolymer.

The sulfonium-type polymers were readily converted into polymer *S*-ylides in dry dimethyl sulfoxide containing potassium *tirt*-butoxide. The ylide reactioned as a nucleophile with benzaldehyde to give styrene oxide.

A cross-linked sulfoxide-type polymer, a polystyrene derivative, containing pendant sulfoxide groups was prepared by the oxidation of *p*-vinylbenzyl methyl sulfide-divinylbenzene copolymer with hydrogen peroxide.

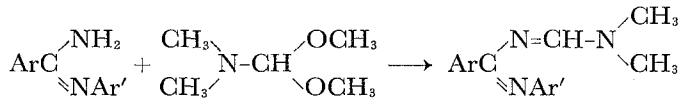
An analogous polymer *S*-ylide could also be prepared from sodium hydride and an oxosulfonium-type polymer, which had been prepared from a sulfoxide-type polymer and methyl iodide. It was noted that styrene oxide could also be obtained from such a polymer *S*-ylide and benzaldehyde.

Some Reactions of N,N-Dimethylformamide Dimethylacetal. M. Nishi, S. Tanimoto, M. Okano and R. Oda. *Yûki Gôsei Kagaku Kyôkai Shi*, **27**, 754 (1969), in Japanese.—Aryl magnesium bromides were treated with N,N-dimethylformamide dimethylacetal (DMFDA) in tetrahydrofuran to obtain the corresponding 1,1-diaryltrimethylamines.



Ar = C_6H_5, *p*-$CH_3OC_6H_4$, *o*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, *o*-$CH_3C_6H_4$

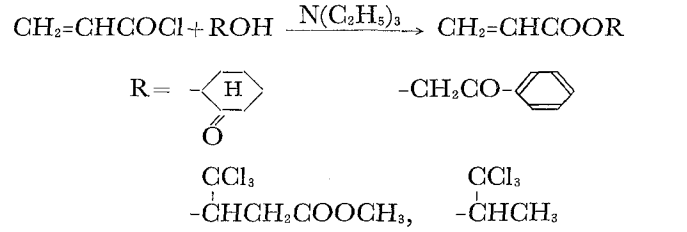
N,-Arylarylamidines reacted with an excess amount of DMFDA to afford the corresponding N-dimethylaminomethylideneamidines, as follows:



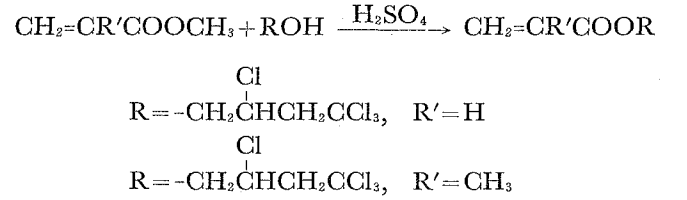
Ar=*p*-$CH_3C_6H_4$ Ar'=C_6H_5, Ar=C_6H_5 Ar'=C_6H_5,
Ar=2-$C_{10}H_7$ Ar'=C_6H_5, Ar=*p*-ClC_6H_4 Ar'=C_6H_5,
Ar=C_6H_5 Ar'=*p*-ClC_6H_4

Condensation reactions of o-aminobenzamide and o-aminobenzenesulfamide with DMFDA or ethyl orthoformate yielded 4-keto-3,4-dihydroquinazoline and 2H-1,2,4-benzothiadiazine 1,1-dioxide, respectively.

Syntheses and Polymerization of Acrylates from Keto Alcohols and Chlorinated Alcohols. M. Nishi, S. Tanimoto, R. Oda and M. Okano. *Yûki Gôsei Kagaku Kyôkai Shi*, **27**, 1235 (1969), in Japanese.—2-Oxocyclohexyl acrylate, phenacyl acrylate, α-trichloromethyl-β-carbomethoxyethyl acrylate and β,β,β-trichloroisopropyl acrylate have been prepared readily by the condensation of acryloyl chloride and the corresponding alcohol with the aid of triethylamine (equation A).



By the alcoholysis of methyl acrylate and methyl methacrylate with 2,4,4,4-tetrachlorobutanol-1, 2,4,4,4-tetrachlorobutyl acrylate and 2,4,4,4-tetrachlorobutyl methacrylate have also been prepared (equation B).



These new acrylates and methacrylate have been polymerized in dioxane using 2,2'-azobisisobutyronitrile as an initiator.

Among others, the Polyacrylates and the polymethacrylates having three to four chlorine atoms in one unit of the polymer chain give films which do not burn.

Kinetics of Liquid Phase Chlorination of Styrene with Cupric Chloride. S. Uemura, Y. Takagaki and K. Ichikawa. *Kôgyô Kagaku Zasshi*, **72**, 2577 (1969), in Japanese.—Kinetics of the chlorination of styrene with cupric chloride in organic solvents have been studied by the initial rate method. In acetonitrile containing lithium

chloride, the reaction rates can be expressed by the equation $v=k_0[CuCl_2]\cdot[Styrene]+k_1[LiCl]\,[CuCl_2]\,[Styrene]$. The reaction is retarded by water, hydrochloric acid and cuprous chloride and accelerated by perchlorate ion. In 1-propanol, the equation is expressed by $v=k_0[CuCl_2]^{1.8}$ [Styrene]. The reaction mechanism has been discussed by considering those kinetic results and the results of synthetic experiments.

Liquid Phase Chlorination of Olefins with Cupric Chloride. K. Ichikawa, S. Uemura, Y. Takagaki and T. Hiramoto. *Bulletin of the Japan Petroleum Institute,* **12**, 77 (1970).—Cupric chloride reacts with gaseous and liquid olefins to form dichloroparaffins in various solvents under milder conditions. Acetic acid containing sodium acetate is the most convenient solvent for the reaction at lower temperatures. The reacting species in this system is found to be CuCl. OAc. NaCl. Acetonitrile containing lithium chloride and various alcohols can also be used as the solvent.

Application of the reaction to butadiene in acetic acid containing sodium acetate has resulted in the formation of 1,4-diacetoxy-2-butene and 3,4-diacetoxy-1-butene.

The kinetics of chlorination of styrene has been studied in acetonitrile-lithium chloride and in *n*-propyl alcohol. On the basis of the rate equation and the structure of the products, the chlorination mechanism and the retarding effect of cuprous chloride are discussed.

Partial Asymmetric Synthesis in α-Alkylation of Enamine with Electrophilic Olefin. K. Igarashi, J. Oda, Y. Inouye and M. Ohno. *Agr. Biol. Chem.,* **34**, 811 (1970).—Partial asymmetric synthesis was obtained in the electrophilic addition of (−)-methyl crotonate (II) to morpholinocyclohexene (I). The levorotatory adduct, (−)-3-3(2-Oxocyclohexyl)butyric acid, was assigned the 3-(*S*)-configuration after the conversion into (−)-3-cyclohexylbutyric acid and comparison with the same enantiomer which in turn was obtained by the conjugate addition of cyclohexylmagnesium bromide to (II) via an established steric course. The Prelog-Cram model is thus applicable to the present system as well.

Self-immolative Asymmetric Synthesis in the Allylic Rearrangement of an Optically Active Amine Oxide. M. Moriwaki, S. Sawada and Y. Inouye. *Chem. Comm.,* 419 (1970).—Transfer of chirality of tetraco-ordinate nitrogen to sp^2-carbon atom was achieved in the thermal [2,3]sigmatropic rearrangement of (+)-*N-trans*-but-2-enyl-*N*-ethyl-*p*-toluidine oxide to (+)-*O*-1-methylprop-2-enyl-*N*-ethyl-*p*-tolylhydroxylamine, whose absolute configuration was correlated with (*S*)-(+)-butan-2-ol. The possible transition state topology was discussed.

Quantitative Determination of Allethrin and Phthalthrin by Gas-liquid Chromatography. N. Baba, A. Nagayasu and M. Ohno. *Agr. Biol. Chem.* **34**, 343 (1970).—A time-saving and accurate method for determining pyrethroids by means of gas-liquid FID-type chromatography was devised. Under the specified conditions, allethrin was determined at so low a concentration as 0.2–1.0 mg/ml with an accuracy of less than ±1% deviation, and this was also the case with phthalthrin at 0.5–1.5 mg/ml concentration. The practical application of this method to some technical pyrethroids products gave satisfactory results of estimation and %-purity of some

technical pyrethroids was determined and it was found that a batch of technical phthalthrin (93.3%) contained 81.5% *trans*-, and 11.8% *cis*-isomers. It was shown that α-DL-*trans*-allethrin and N-(3,4,5,6)-tetrahydrophthalimidomethyl (±)-*trans*-chrysanthemate can be used as an internal standard to each other.

Terpenoids—XII. The Stereochemistry of Some Alcohols Derived from Enmein. E. Fujita, T. Fujita, and Y. Nagao. *Tetrahedron,* **25**, 3717 (1969).—The reduction of a diketolactone ester derived from enmein, a major bitter diterpene of *Isodon trichocarpus,* with $LiAl(t\text{-}BuO)_3H$ in absolute tetrahydrofuran gave two diols, both of which on weak alkaline treatment afforded epimerized alcohols. A ketolactone ester, another derivative of enmein, was reduced with $LiAl(t\text{-}BuO)_3H$ in anhydrous solvent to give an alcohol, while it was reduced with $NaBH_4$ in MeOH-H_2O to give another epimeric alcohol. The former alcohol was epimerized to the latter in weak alkaline conditions. Two other epimeric alcohols were derived from the latter *via* a series of reactions. The similar epimerization between the last epimers was also recognized. The absolute configuration of all the epimeric alcohols was unambiguously established.

Terpenoids. XIII. Thin-Layer Chromatography of Several Epimeric Enmein Derivatives. E. Fujita, T. Fujita, and Y. Nagao. *Yakugaku Zasshi,* **89**, 1125 (1969), in Japanese.—Silica gel thin-layer chromatography of 16 kinds of epimeric enmein derivatives was investigated. Compounds possessing a β-OH group at C-15 (numbering of enmein) were shown to be more easily adsorbed than compounds possessing an α-OH group at C-15. The unfavorable influence of C-16 β-methyl group for adsorption was recognized. The most favorable effect for adsorption was provided by C-3 α-equatorial OH among the compounds with a double bond at C-1 (C-2).

Terpenoids—XIV. Formal Chemical Conversion of Enmein into *ent*-Kaurene, Atisine, Garryine, and Veatchine. E. Fujita, T. Fujita, and H. Katayama. *Tetrahedron,* **26**, 1009 (1970),—A lactone ester derived from enmein was subjected to acyloin condensation. The desired main product was converted into an important hemiketal diol, which had been converted into *ent*-kaurene, atisine, garryine, and veatchine, *via* a series of reactions. Thus, the work constitutes a formal chemical conversion of enmein into *ent*-kaurene and the foregoing diterpene alkaloids.

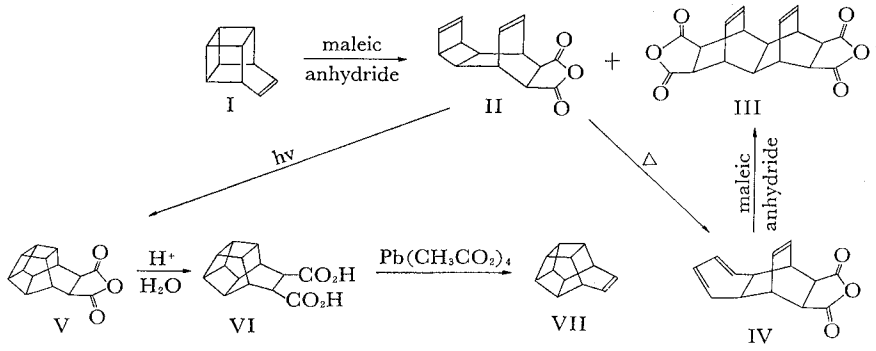
The Structure and Absolute Configuration of Sodoponin and Epinodosinol, New Minor Diterpenoids of *Isodon Japonicus*. E. Fujita, T. Fujita, M. Taoka, H. Katayama and M. Shibuya. *Tetrahedron Letters, 421,* (1970).—Two new minor diterpenoids, sodoponin and epinodosinol, were isolated from the leaves of *Isodon japonicus,* and their structure and absolute configuration were determined on the basis of the spectroscopic and chemical evidence. Finally, sodoponin was converted into epinodosinol by its treatment with metaperiodate followed by hydrolysis.

Polymerization of Allene with Nickel (II) Phosphine Complexes. S. Kunichika, Y. Sakakibara and T. Okamoto. *Kôgyô kagaku zasshi,* **72**, 1814 (1969), in Japanese.—The polymerization of allene has been carried out by using the bis

(triphenylphosphine)nickel(II)halide catalysts. The reaction proceeded smoothly in aromatic or halogenated hydrocarbons under pressure at 90°C and produced polyallene $\dagger CH_2\text{-}C(=CH_2)\dagger_n \dagger C(=CH_2)\text{-}CH_2\dagger_m$. Strong donor solvents were not good for the polymerization. Introduction of an electron releasing group in the *para* position of aryl groups in the catalyst had little influence on the reaction. Changing halogen atoms of the catalyst, the yield increased greatly in the order of Cl<Br<I. Some kinetic study of the reaction showed that the polymerization was first order with respect to allene, and to catalyst. When low concentrations of allene were used, a nickel mirror appeared on the side wall of the reaction tube. From these data, the low valent nickel complexes, which may be produced from allene and catalyst, are considered to play a role as active species for the polymerization.

Electrocyclic Additions to Pentacyclo [4.4.0.0^{2,5}.0^{3,8}.0^{4,7}] deca-9-ene[1]. E. LeGoff and S. Oka. *J. Amer. Chem. Soc.*, **91**, 5665 (1969).—Maleic anhydride adds to the title compound I forming the 1 : 1 adduct II and the 2 : 1 adduct III. Heating II opens the cyclobutene ring and affords the triene IV. Heating IV with maleic anhydride yields III.

Photochemical ring closure of the diene II affords the hexacyclic V. Bisdecarboxylation of the diacid VI affords the hexacyclic olefin VII.



If tetracyanoethylene is used in place of maleic anhydride in the sequence of reactions just described an analogous series of compounds can be synthesized.

Polymer Chemistry

Thermodynamic and Conformational Properties of Styrene-Methyl Methacrylate Block Copolymers in Dilute Solution. I. Preparation and Characterization. H. Ohnuma, T. Kotaka and H. Inagaki. *Polymer*, **10**, 501 (1969).—An anionic polymerization procedure for preparing styrene and methyl methacrylate block copolymers is described. The products were characterized by combustion analysis, osmometry, light scattering measurement, and gel permeation chromatography. The analyses showed that the block copolymers consisted of linear three-block chains except for a few cases. The correlation between the heterogeneities of molecular weights and of composition as described by light scattering apparent molecular weights in different solvents is discussed. The heterogeneities can be described by two para-

meters for the polydispersities of precursor polystyrene and poly(methyl methacrylate) subchains and by the average composition of the block copolymer. Preliminary data on the light scattering conformational analyses are given. The results suggest that the block copolymer chains would assume the conformations similar to any flexible linear homopolymers at least in the solvents, toluene and butanone, examined in this study.

Thermodynamic and Conformational Properties of Styrene-Methyl Methacrylate Block Copolymers in Dilute Solution. II. Behavior in Theta Solvents. T. Kotaka, H. Ohnuma and H. Inagaki. *Polymer,* **10,** 517 (1969).—To find θ solvents for random and block copolymers of styrene and methyl methacrylate, various solvents were examined by the cloud point test. From among the solvents examined, cyclohexanol and 2-ethoxyethanol were chosen and the θ temperatures were determined by osmotic pressure measurement. In cyclohexanol two homopolymers have almost equal θ, to which the θs of the block copolymers are also quite close; while the θs of the random copolymers show a minimum at nearly equimolar composition.

Intrinsic viscosities $[\eta]$ of nearly equimolar block copolymers were examined in these two θ solvents. In contrast to random copolymers the $[\eta]_\theta$ of the block copolymers are sensitive to the type of θ solvent employed. From $[\eta]_\theta$ data in cyclohexanol the unperturbed mean square radius of gyration for the block copolymers was estimated as $10^{18} <s>_0/M_w^{1/2}=6.35(\mathrm{cm}^2)$ which is better approximated by the simple composition average of the parent homopolymers as previously suggested by Stockmayer. The behavior of the block copolymers in a good solvent, toluene, was compared with that of the random copolymers and the homopolymers: the $[\eta]$s are smaller than those of the corresponding random copolymers but are about the average of the two homopolymers. An anomaly in $[\eta]$ which was often suggested as that due to 'intrachain phase separation' in block copolymer chains was not observed.

Dilute Solution Properties of Styrene-Methyl Methacrylate Copolymers with Different Architecture. T. Kotaka, T. Tanaka, H. Ohnuma, Y. Murakami and H. Inagaki. *Polymer Journal,* **1,** 245 (1970).—The results of an extensive study on solution properties of alternating, statistical and block copolymers of styrene and methyl methacrylate with nearly equimolar composition are described, by placing emphasis upon their dependence on the sequential arrangement of monomers. The θ temperatures are determined in cyclohexanol by a phase-equilibrium method. Measurements of intrinsic viscosity are made in six different solvents, which are chosen to differ in their behavior toward the parent homopolymers. All data are examined on the basis of current two parameter theories.

The short-range interactions, as given by the characteristic ratios, are expressed for the block copolymers as a composition average of those of the parent homopolymers, whereas for the alternating and statistical copolymers they show a positive deviation from the average. The deviation is roughly proportional to the population of the dyads of unlike monomers in the copolymer chain, *i.e.,* to the run number. The long-range interactions are interpreted by assuming dyads as copolymer segments. Thus, the interaction parameters of the statistical and block copolymers may be expressed as a function of composition and run number in terms of the three parameters each char-

acterizing the interaction of the parent homopolymers and the alternating copolymer with the pure solvent.

Determination of Compositional Heterogeneity in Copolymers by Thin Layer Chromatography. II. Effects of Monomeric Arrangements on Chromatographic Separation. F. Kamiyama, H. Matsuda, and H. Inagaki. *Makromolekulare Chemie,* **125**, 286(1969), in Germany.—Block, statistical, and alternating copolymers of styrene and methyl methacrylate are subjected to thin layer chromatography combined with concentration gradient development using chloroform and ethyl acetate. It is found that first the statistical polymer, and later the alternating polymer, were developed, while the block polymer remained on the starting line. This result has been explained in terms of the differences in the forces of adsorption onto the stationary phase which are associated with three types of dyads in the copolymer chain, viz., A-A, A-B, and B-B.

Separation of Stereospecific Polymers with Respect to Their Steric Isomerism by Thin Layer Chromatography. H. Inagaki, T. Miyamoto and F. Kamiyama. *J. Polymer Sci.*, **7**, 329 (1969).—Thin layer chromatography is utilized to explore the separation characteristics of isotactic and syndiotactic poly[methyl methacrylate] and mixtures of these. It is found that ethyl acetate yields different R_f values (rate of flow) for isotactic, syndiotactic, and atactic polymers; the isotactic polymer remains on the starting line, while the syndiotactic and atactic polymers reach the neighborhood of the solvent front. The possibility for a quantitative determination of amounts of separated components on chromatogram is discussed.

Thin Layer Chromatographic Studies on Specific Interactions between Stereoisomeric Chains of Poly(Methyl Methacrylate). T. Miyamoto and H. Inagaki. *Macromolecules,* **2**, 554 (1969).—The stereocomplex formation between isotactic and syndiotactic poly (methyl methacrylate) chains is studied by using thin layer chromatography and high resolution NMR. Stereocomplex formation was achieved by admixing the stock solutions of the two stereoregular polymers in three different ratios, namely 2 : 1, 1 : 1, and 1 : 2 (iso/synd). It is concluded that the 1 : 1 mixture forms the primary structure; while the 1 : 2 complex the secondary structure which is composed by association between the primary structure and the syndiotactic polymer molecules.

The Stereocomplex Formation in Poly (Methyl Methacrylate) and the Stereospecific Polymerization of its Monomer. T. Miyamoto and H. Inagaki. *Polymer Journal,* **1**, 46 (1970).—The stereocomplex formation between isotactic and syndiotactic poly(methyl methacrylate) (PMMA) molecules is studied in detail, using the techniques of thin layer chromatography (TLC), ultracentrifugation, x-ray diffraction, viscometry, and high-resolution NMR. It is shown that the 1 : 1 (iso/synd) complex is formed as the primary structure; further associations between the 1 : 1 complex and free syndiotactic molecules, when they exist in solution, occur to form the 1 : 2 (iso/synd) complex.

The so-called "stereoblock" PMMA samples prepared with *n*-butylmagnesium chloride and diphenylmagnesium are analyzed by using the technique. Evidence is thus shown for the stereochemical identity between the stereoblock PMMA and the stereocomplex which is formed by isotactic and syndiotactic PMMA in the ratio 1 : 2 (iso/synd). On the basis of this result, we conclude that the 1 : 2 stereocomplex may be formed during stereospecific polymerization of methyl methacrylate (MMA) with different Grignard's types of catalysts.

In relation to the above conclusion stereospecific polymerizations of MMA at −50°C with *n*-butylmagnesium chloride in toluene were carried out in the presence of either isotactic or syndiotactic PMMA. The results suggest that the stereospecific polymerization of MMA is closely linked to the stereocomplex formation. The presence of the isotactic polymer chains promotes preferentially the polymerization of MMA to the syndiotactic polymer chains, while the presence of the syndiotactic polymer chains appears to be a prerequisite for initiating the polymerization to the isotactic polymer chains so far as this catalytic system is employed at −50°C.

Structural and Steric Isomerism of Polypropylenes T. Miyamoto and H. Inagaki. *J. polymer Sci., Part A-2,* **7**, 963 (1969).—The structural and steric isomerism of propylene polymers has been estimated on the basis of solution properties as well as infrared and high-resolution nuclear magnetic resonance spectra. Three general types of polypropylenes were prepared: polymers prepared with the cationic catalytic system $AlCl_3$-C_2H_5Cl, stereoblock polymers obtained by successive extraction from a commercial product and isotactic polymers of low molecular weight obtained by thermal degradation of a highly isotactic polymer followed by hydrogenation with Adam's catalyst in dioxane at 40°C. The characterization of all samples was accomplished by equilibrium ultracentrifugation, vapor-pressure osmometry, viscometry, and gel-permeation chromatography. It is found that the molecular chain of cationically prepared polymer is somewhat branched owing to structural isomerism during polymerization. Isoamyl acetate is found to be a theta solvent for stereo-block as well as for atactic and syndiotactic polymers; the theta temperature is determined as the temperature at which the light-scattering second virial coefficient A_2 vanishes. A close correlation is found between the theta temperature and stereoisomerism. The absorbances of the 1154 and 974 cm^{-1} bands in the infrared spectra decrease with decreasing molecular weight; in addition to the mere existence of alternating CH_2 and $CH(CH_3)$ groups in the polymer chain, rather long sequences of this type are required for the appearance of these bands. Changes in the absorption band at 997 cm^{-1} show that chains consisting of over ten isotactically connected monomer units can assume a helical conformation. From the high-resolution NMR spectra of different polypropylenes, including isotactic polymers of low molecular weight, it is found that in estimating the microstructure, account must be taken of the effects of stereoisomerism within tetrads of monomer units on the apparent widths of the methylene proton resonances. If substantial concentrations of several of the possible types of tetrads are present (*i.e.*, if the tactic sequence lengths are quite short), then it is difficult to determine the relative amounts of tactic dyads accurately from the 100 Mcps methylene proton resonances.

Shear-Rate Dependence of the Intrinsic Viscosity of Flexible Linear Macromolecules. II. Solvent Effect. H. Suzuki, T. Kotaka, and H. Inagaki. *J. Chem. Phys.*, **51**, 1279 (1969).—Measurements of the shear-rate dependence of the intrinsic viscosity $[\eta]$ were made on polystyrenes in several solvents, each of which differs in solvent power and solvent viscosity. Low-shear capillary viscometers of the Maron-Belner type were used: shear stresses can be varied continuously from about 10 to a few tenths of a dyn/cm^2, which is low enough to measure the zero-shear intrinsic viscosity $[\eta]_0$. The effect of excluded volume on the behavior of $[\eta]/[\eta]_0$-*vs*-β (the generalized shear-rate) curve was examined. The curves at and near the θ condition resemble that of Saito-Scheraga's prolate ellipsoid with axial ratio $p=2$, and those in good solvents resemble that of $p=3$ ellipsoid; the variation with solvent power is not so large as the theory of either Fixman or Chikahisa predicts. In the region of moderate to large β, the $[\eta]/[\eta]_0$-*vs*-β curve decreases continuously with increasing β, as contrasted to the behavior of the ellipsoid, which levels off rather rapidly. The non-Newtonian behavior is practically unaffected by solvent viscosity. In addition, the effect of polydipersity was discussed briefly.

Excluded Volume in Flexible Linear Macromolecules. H. Suzuki. *Macromolecules*, **3**, 373 (1970).—The effect of excluded volume in flexible linear macromolecules is treated with the Fixman differential equation approach. The equation is solved in the uniform-expansion approximation by use of the recent results of perturbation theories. The results are as follows:

$$\alpha_R^2 = 0.572 + 0.482(1 + 6.23z)^{1/2}$$
$$\alpha_S^2 = 0.609 + 0.391(1 + 6.53z)^{1/2} .$$

Here α is the expansion factor; the subscripts R and S refer to the end-to-end distance and the radius of gyration, respectively; z is the excluded-volume variable. These equations are discussed in comparison with others derived with different approaches.

Dilute Solution Properties of Polyvinyl Butyral. H. Matsuda, K. Yamano and H. Inagaki. *Kôgyô Kagaku Zasshi*, **73**, 390 (1970).—Viscosity measurements of polyvinyl butyral (PVB) have been made in various solvents. The molecular weight determination of PVB was made mainly in ethanol by light scattering and in dioxane by osmometry. The apparent molecular weights for PVB determined by light scattering depended considerably on the refractive indices of solvents used. This fact suggests that PVB samples have remarkable heterogeneities in chemical composition. It was found that PVB has a tendency to association in dilute solution at room temperature, and contains microgels and branched chains. The average branch numbers for some PVB samples determined both from viscosity and molecular weight measurements agreed with each other.

In addition, the unperturbed chain dimensions $(\langle L^2\rangle_0/P)^{1/2}$ (P: degree of polymerization) were estimated according to the Stockmayer-Fixman equation and the effect of an acetal ring and the configuration of the original polyvinyl alcohol (PVA) upon chain flexibility was discussed. The values of $(\langle L^2\rangle_0/P)^{1/2}$ for PVB chains derived from atactic PVA and isotactic PVA were 6.5~6.7 and 5.98 Å, respectively. On this basis, it is concluded that PVB assumes a more extended configuration than

PVA does due to the formation of an acetal ring, and the chain flexibility of isotactic PVB is higher than that of atactic PVB.

Unperturbed Dimension of Poly(butylene oxide). M. Matsushima, M. Fukatsu and M. Kurata. *Bull. Chem. Soc. Japan,* **41**, 2570 (1968).—Viscosity and light scattering measurements of poly (butylene oxide) were carried out in various solvents, including a theta solvent, isopropanol. The intrinsic viscosity *vs.* molecular weight relationships obtained in the range of molecular weight from 2.1×10^5 to 2.3×10^6 were:

$[\eta]=3.39\times10^{-5}\ M_w^{0.84}$ in benzene at 30°C,
$[\eta]=4.08\times10^{-5}\ M_w^{0.79}$ in methyl ethyl ketone at 30°C
$[\eta]=8.65\times10^{-4}\ M_w^{0.50}$ in isopropanol at 29.8°C.

The ratio σ between the end-to-end distance of the polymer chain in the unperturbed state and that in the freely rotating state was estimated to be 1.66.

Dilute Solution Properties of Monodisperse Poly (α-methyl styrene). I. Sedimentation Coefficient in Theta Solvent. M. Abe, K. Sakato, T. Kageyama M. Fukatsu and M. Kurata. *Bull. Chem. Soc. Japan,* **41**, 2330 (1968).—The sedimentation behavior of anionically polymerized poly (α-methyl styrene) has been studied as a function of molecular weight, concentration and speed of centrifugation under the theta condition of solvent and temperature, *i.e.,* in cyclohexane at 39°C. Analysis of the data was made by use of Fujita's equation for the pressuer- and concentration-dependent sedimentation. It was found that the sedimentation coefficient at zero concentration and one atmosphere was given as $s_0^0=2.00\times10^{-15}\ M^{1/2}$ sec, where M is molecular weight. The concentration dependence coefficient k and the pressure dependence coefficient μ appearing in the Fujita equation were obtained as $k=6.2\times10^{-4}\ M^{1/2}$ dl/g, and $\mu=1.6\times10^{-9}$ cm^2/dyne, respectively. The intrinsic viscosity in the theta solvent was also determined as $[\eta]_\theta=7.60\times10^{-4}\ M^{1/2}$ dl/g.

Excluded Volume Effect of Linear Polymer Molecules. M. Kurata. *J. Polymer Sci, A-2,* **6**, 1607 (1968).—An approximate closed expression for the excluded volume effect of linear polymer molecules is developed with the aid of a uniform expansion model of perturbed chains. The linear expansion factor α for the end-to-end distance is given by $(\alpha^3-1)+(3/8)(\alpha^5-\alpha^3)=(5/2)z$ where z is the excluded volume parameter. This equation is numerically close to the Ptitsyn equation in the ordinary range of α; *i.e.,* for $1\leq\alpha\leq2$.

Dilute Solution Properties of Monodisperse Poly (α-Methylstyrene) II. Hydrodynamic Properties in Good Solvents. K. Sakato and M. Kurata. *Polymer J.,* **1**, 260 (1970).—Hydrodynamic properties of monodisperse poly (α-methylstyrene) were studied in dilute benzene solutions, both concentration and molecular weight being varied. Molecular weight determination was performed by three methods, osmometry, light scattering and sedimentation equilibrium. The intrinsic viscosity was found to be $[\eta]=(1.03_4\pm0.05)\times10^{-4}\ M^{0.72}$ dl/g at 30°C, where M is the molecular weight. The sedimentation coefficient extrapolated to zero concentration and

one atmosphere was found to be $s_0^0=(3.61\pm0.03)\times10^{-15}\ M^{0.43}$ sec. The Scherage-Mandelkern constant β was evaluated as $(2.43\pm0.03)\times10^6$ which was independent of M and in agreement with the value previously obtained in theta solvent. The concentration dependence of sedimentation coefficient was found to be compatible with the recent theory by Pyun and Fixman.

Viscoelastic Properties of Monodisperse Polymers. I. Tensile Creep Studies of Poly (α-Methylstyrene). H. Odani, N. Nemoto, S. Kitamura, M. Kurata and M. Tamura. *Polymer J.*, **1**, 356 (1970).—Tensile creep measurements were made on seven monodisperse polymer samples of poly (α-methylstyrene) ranging in molecular weight from 69000 to 1740000. The temperature dependence of the tensile creep compliance was described by the method of reduced variables, and the shift factors were identical for all samples, except for those on the level of glassy hardness. The steady-state compliance and tensile viscosity were determined by used the extrapolation method of Ninomiya. It was shown that the dependence of these quantities on molecular weight is much different from that predicted by the Rouse-Bueche theory or by the semi-empirical Ferry-Landel-Williams theory. That is, in the region of molecular weight somewhat above the entanglement region the steady-state compliance is independent of molecular weight. At lower molecular weights the values of the steady-state compliance increase with decreasing molecular weight. The dependence of tensile viscosity on molecular weight follows the familiar 3.4 power law up to molecular weight of about 2×10^5, but there is a distinct decrease in the viscosity dependence upon molecular weight at higher molecular weights. The value of the average molecular weight between entanglements was derived from tensile creep compliance versus temperature curves by use of a reference value of time equal to 1000 sec. The value evaluated decreased with increasing molecular weight up to about 2×10^5 and then leveled off to a certain constant value.

Low Angle, Light Scattering Photometer Model LS-2. H. Utiyama and Y. Tsunashima. *Appl. Optics*, **9**, 1330 (1970).—A light scattering instrument capable of routine measurements at angles as low as 9° is described. The reduced scattered intensities can be determined, with use of a vertically polarized incident light, correct to 0.5~1.0%, unless the scattering of the solution over solvent is less than $10^{-5}\ cm^{-1}$. The correction for the back reflection of the incident beam can be ignored because the light is absorbed by a glass neutral filter before it reaches a glass-air interface. A sample liquid can be brought to a temperature equilibrium in less than 30 min, and the temperature can be kept constant within ±0.02°C, in the temperature range from 5°C to 100°C. No special optical specification is required in making a cell, and the geometrical correction is simply given by $\sin^{-1}\theta$ correct to $\pm0.7\%$.

Normal Stress Effect of Dilute Polymer Solutions. III. Monodisperse Poly-α-methylstyrene in Chlorinated Biphenyl. K. Osaki, K. Sakato, M. Fukatsu, M. Kurata, K. Matusita, and M. Tamura. *J. Phys. Chem.*, **74**, 1752 (1970).—The normal and shear stresses in steady shear flow were measured on dilute solutions of monodisperse poly-α-methylstyrene in two chlorinated biphenyls. The zero-shear viscosity η and the reduced steady shear compliance γ were evaluated from these

measurements as functions of concentration and molecular weight. The intrinsic viscosity of the polymer in the chlorinated biphenyls was found to be very close to that in benzene, a good solvent. In the limit of zero concentration, the γ value was about 0.20 irrespective of the molecular weight. The quantity increased with concentration and attained to a value as high as 0.7 which exceeds the value 0.40 corresponding to the so-called free-draining limit. It is concluded from this evidence that the polymer chain behaves as a nondraining coil at infinite dilution and that the increase in γ with concentration does not arise from a decrease in the hydrodynamic interaction of the segments.

Flow Properties of Moderately Concentrated Solutions of Polystyrene in Chlorinated Diphenyl. K. Osaki, M. Kurata and M. Tamura. *Polymer J.*, **1**, 334 (1970).—Flow properties such as complex moduli, complex moduli with superimposed steady shear and non-Newtonian viscosity were measured on moderately concentrated solutions of polystyrene in chlorinated diphenyl. The range of molecular weight M and of concentration c was $5.6\times10^5-2.5\times10^6$ and $1-4.5$ g/dl, respectively. The real part G' and the imaginary part G'' of the complex modulus of solutions with various molecular weights and concentrations were superimposed to give single composite curves, respectively, if $G'M$ and $G''M$ were plotted against $\omega\eta$M, where ω is the angular frequency and η is the zero-shear viscosity. Thus the steady shear compliance J_e is proportional to M and is independent of c. The values of the real part G' and the imaginary part G'' of the complex moduli with superimposed shear decreased when the rate of superimposed shear κ increased. They decreased more rapidly in the range low of frequency that in the range of high frequency. The degree of decrease was higher for the real part than for the imaginary part. This effect of the superimposed steady shear on the complex moduli, together with the molecular weight and concentration dependence of the complex moduli, were qualitatively interpreted by assuming molecular aggregates in moderately concentrated polymer solutions.

Viscoelastic Properties of Narrow-Distribution Polymers. I. Tensile Creep Studies of Polystyrene. N. Nemoto. *Polymer J.*, **1**, 485 (1970).—Tensile creep measurements were made on seven narrow-distribution polystyrene samples. The range of molecular weights was from 7.50×10^4 to 2.90×10^6 and that of temperature from 96 to 198°C. The data were all reduced to 140°C by the method of reduced variables. The shift factors were identical for all samples and followed the WLF equation. The free volume parameters were calculated by the method of Williams; the fractional free volume at T_g was 0.028 and the constant B in the Doolittle equation was 0.97. In the transition zone, all master curves, except that of the highest molecular-weight sample L-1, coincided. The master curve of sample L-1, shifted to the right on the logarithmic time scale by a factor of about 0.6, compared with those of other samples, and the retardation spectrum $L(\tau)$ disappeared in the rubbery zone. A close relationship between these two observations was suggested. The average molecular weight between entanglements was independent of molecular weight as evaluated by ordinary methods. The dependences on molecular weight of the quantities, ηl, D_e and τ_m, were also examined. It was found that ηl and τ_m varied as 3.3 powder of molecular weight and D_e was independent of molecular weight.

Crystallization of Sheared Polymer Melts. K. Kobayashi and T. Nagasawa. *J. Macromol. Sci. Phys.* **B4(2)**, 331 (1970).—The crystallization kinetics of molten polyethylene subjected to a constant shear stress were investigated theoretically and experimentally. The rate of crystallization depends on the difference of entropy (Δs) between the crystalline and molten state. The constant shear stress in the melt decreases Δs causing an abrupt increase in the rate of crystallization and a decrease of the thickness of the folded-chain lamellar crystals.

Graft Copolymerization of Acrylamide onto ^{60}Co γ-ray Pre-irradiated Cotton Fabrics in Aqueous Dioxane and Some Textile Properties of the Grafted Cotton Fabrics. T. Ikeda, M. Hamanaka and W. Tsuji. *Sen-i Gakkaishi,* **25**, 447 (1969), in Japanese.—Graft copolymerization of acrylamide onto the ^{60}Co γ-ray pre-irradiated cotton fabrics was investigated in various water-dioxane mixtures. The effects of the grafting mediums on the swelling behavior of the fabrics, degree of grafting or dimensional stability of the grafted fabrics was also studied.

Degree of swelling of the cotton fabric in aqueous dioxane and 15% acrylamide aqueous dioxane solution where water contents are 20~80% shows higher values than those in water or dioxane alone. Absorbed monomer content in the cotton fabrics from the monomer solutions is almost constant and independent of the composition of the mediums and the degree of swelling of the fabrics. Degree of grafting is nearly constant up to 50% dioxane content in the grafting mediums and then a significant decrease is observed, while the rate of the catalyzed solution polymerization of acrylamide gradually decreases with increasing dioxane content in the polymerization mediums with the exception of the medium containing 10~30% water content. Cotton fabrics which were grafted in relatively higher swelling media show less dimensional stability during grafting and hot water extraction, and the conditioned tensile strength of warp of the fabrics appears to be slightly higher than those obtained in less swelling media.

Biochemistry

Electron Microscopic Studies on the Crystal Structure of Tropomyosin. S. Higashi Fujime and T. Ooi. *Journal de Microscopie,* **8**, 535 (1969).—Crystal structures of tropomyosin, which is a rod-like protein, were investigated by electron microscopy. The three-dimensional crystal (Form I) is constructed by layers of the network of a tetragon whose sides are 220 Å and 182 Å long. This form belongs to space group $P2_12_12$. Cell dimensions are 243 Å, 313 Å and about 70 Å for the a-, b-, and c- axes, respectively. The length of molecular unit is 400 Å, a half of which is the asymmetric unit. Molecules connect at midpoints of the shorter sides of the tetragon. In the two-dimensional square lattice with 400 Å space (Form IV), molecules connect at midpoints of the sides. The length of the asymmetric unit and the molecular unit are the same as those for Form I. Antiparallel arrangement of molecules is expected in the molecular unit. A new form of hexagonal lattice with 400 Å space (Form III) was found. Dislocation and coexistence of different phases in a crystal were directly observed.

The Reductive Conversion of N-Terminal Pyroglutamyl into Prolyl Residues in Polypeptides and Proteins. S. Takahashi and L. A. Cohen. *Biochem.* **8**, 864 (1969).—The pyrrolidone ring of an N-terminal pyroglutamyl residue in a polypeptide or protein may be converted by reduction with diborane into a pyrrolidine ring. Thus, the originally nonbasic N-terminal residue is identified by its conversion into proline. Diborane reduction offers a rapid and facile means of demonstrating the presence of an N-terminal residue of pyroglutamic acid and of initiating sequential analysis of the polypeptide chain. Bovine γ-globulin was shown to have an N-terminal pyroglutamate by this method.

Titration of Ribonuclease T_1. S. Iida and T. Ooi. *Biochem.*, **8**, 3897 (1969).—The results of potentiometric and spectrophotometric titrations on RNase T_1 solutions suggest the following conclusions: nine out of twelve side chain carboxyl groups have an abnormally low pK_0 of 3.85, and the other three have a high one of 5.3; the three imidazol groups can be classified into two sets, two groups with $pK_0=6.6$ and one with $pK_0=7.4$; only two of the nine phenolic groups titrate normally. Titrations in the presence of an inhibitor, 2′GMP, show that over the pH region 5–9 fewer groups ionize in the complex than in the free protein. The difference titration curve for RNase T_1 and 2′-GMP complex has a maximal volve of ca. 1 mole of hydrogen ion/mole of protein at pH 6.3, which can be interpreted as reflecting a shift in the pK of one group from 4.9 to 7.8, and therefore as suggesting that one carboxyl group, presumably Glu-58, is masked by binding of the inhibitor.

The Facilitation of $NaBH_4$ Reduction of Esters of Phenols and of Acidic Alcohols. S. Takahashi and L. A. Cohen. *J. Org. Chem.*, **35**, 1505 (1970).—The reduction of esters (RCOOR′) by $NaBH_4$ is facilitated by use of R′ more electronegative than methyl, rate enhancements of at least 300 fold demonstrated. The rates of reduction of substituted phenyl esters correlated linearly with the pKa of the corresponding phenols ($\rho=2.6$), a separate correlation being obtained for alcohols. The difference was ascribed to conformational or steric obstruction by the aromatic ring; furthermore, reduction is significantly faster in media containing water. By use of an appropriate alcohol for esterification, carboxyl groups can be reduced selectively to primary alcohols in the presence of functional groups which are reactive toward more powerful reducing agents.

The Synthesis of Regular Copolymers of Glycide and Alanine. S. Takahashi. *Bull. Chem. Soc. Japan.*, **42**, 521 (1969).—The synthesis of polypeptides with a repeating sequence of Gly and L-Ala, *i.e.*, $(\text{L-AlaGly}_2)_n$, $(\text{L-Ala}_2\text{Gly})_n$, $(\text{L-Ala}_3\text{Gly})_n$, are reported. Polymerization was achieved by a self-condensation of p-nitrophenyl esters of the corresponding tri- or tetrapeptides.

Conformation of Sequential Polypeptides Containing L-Alanyl and Glycyl Residues. T. Iio and S. Takahashi. *Bull. Chem. Soc. Japan*, **43**, 515 (1970).—The conformations of four polypeptides containing ordered sequences of L-Ala and Gly residues, $(\text{Ala})_n$, $(\text{Ala}_3\text{Gly})_n$, $(\text{Ala}_2\text{Gly})_n$, and $(\text{AlaGly}_2)_n$, are investigated in solution. ORD and IR showed all the polymers assume both an α-helix and a β-conformation

in solution. The stability of the α-helix decreases in the order: $(Ala)_n$, $(Ala_2Gly)_n$, $(Ala_3Gly)_n$, and $(AlaGly_2)_n$; this may be explained in terms of the interaction between methyl groups of L-Ala residues regularly arranged on the surface of the α-helix.

A New Spectrophotometric Method for Determination of D-Amino Acids, Pyridoxal, and Pyridoxal Phosphate. K. Soda, T. Osumi, T. Yorifuji, H. Misono and M. Moriguchi. *Amino Acid and Nucleic Acid,* **21**, 89 (1970), in Japanese.—(1) A simple and rapid technique for the determination of the D-amino acids which are oxidized by D-amino acid oxidase has been presented. This method involves an oxidation of D-amino acids with D-amino acid oxidase in the presence of catalase, and the spectrophotometric determination of the resultant α-keto acids with 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH). The additions of L-amino acids have no influence on the quantitative estimation of D-amino acids in the presence of the L-isomers, and also is applicable for the determination of D-amino acid oxidase activity.

(2) A spectrophotometric method with MBTH was also developed for the determination of pyridoxal and pyridoxal phosphate, and for the selective determination of each in the presence of the other. Pyridoxal and pyridoxal phosphate react with the reagent to yield the azine derivatives, which give characteristic absorption spectra. The highest absorbance values are obtained when pyridoxal and pyridoxal phosphate are incubated at pH values of about 3.4 and 8.0, respectively; their maxima are at 430 and 380 mμ, respectively.

The azine of pyridoxal is only slightly soluble under the neutral and alkaline conditions, whereas that of pyridoxal phosphate is substantially insoluble in the acid pH range. This difference in solubility of the azines made possible the selective determination of pyridoxal and pyridoxal phosphate. α-Ketoglutarate and pyruvate are among the substances shown not to interfere with the assay of pyridoxal; their derivatives absorb appreciably only at wavelengths below 420 mμ. For the assay of pyridoxal phosphate in the presence of these compounds measurement at 390 mμ is necessary.

N-Acetylation of an L-Lysine Antagonist, S-(β-Aminoethyl)-L-Cysteine by *Aerobacter Aerogenes*. K. Soda, H. Tanaka and T. Yamamoto. *Amino Acid and Nucleic Acid*, **21**, 56 (1970), in Japanese.—*Aerobacter aerogenes* was found capable of growing well in the medium containg S-(β-aminoethyl)-L-cysteine, a metabolic antagonist of L-lysine, as a sole nitrogen source. The metabolic product has been isolated, purified, and identified as S-(β-N-acetylaminoethyl)-L-cysteine by comparison with the synthetic compound on the basis of studies by paper electrophoresis, paper and ion-exchange chromatographies, nuclear magnetic resonance spectroscopy, infrared spectrophotometry, x-ray diffraction, absorption spectrophotometry of ninhydrin color, elemental analysis, optical rotation, and reaction with L-lysine decarboxylase.

The metabolic function of this N-acetylation is discussed.

Enzymic *N*-Acetylation of a Sulfur Analog of L-Lysine, *S*-(β-Aminoethyl)-L-Cysteine. K. Soda, H. Tanaka and T. Yamamoto. *FEBS Letters,* **8**, 301 (1970).—It is Known that *S*-(β-aminoethyl)-L-cysteine termed also L-thialysine, inhibits the growth of lactic acid bacteria as a potent antimetabolite of L-lysine. *Aerobacter aerogenes* was found to be capable of growing well in the medium containing this L-lysine antago-

nist as a sole nitrogen source, and the metabolic product has been isolated and identified as *S*-(*β*-*N*-acetylaminoethyl)-L-cysteine. Enzymatic incorporation of the radioactivity into *S*-(*β*-*N*-acetylaminoethyl)-L-cysteine from *S*-(*β*-amino-ethyl)-L-cysteine, and studies on acetyl donor specificity indicate occurrence of an enzyme in the cell-free extract of *Aerobacter aerogenes,* which catalyzes the transfer of acetyl group from acetyl-CoA to the terminal amino group of *S*-(*β*-aminoethyl)-L-cysteine as follows.

$$NH_2 \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH(NH_2) \cdot COOH + CH_3 \cdot CO\text{-}CoA$$

$$\downarrow$$

Acetyl-CoA : S-(*β*-aminoethyl) L-cysteine *ε*-*N*-acetyltransferase.

$$CH_3 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH(NH_2) \cdot COOH + CoA.$$

Spectrophotometric Determination of Pyridoxal and Pyridoxal 5′-Phosphate with 3-Methyl-2-Benzothiazolone Hydrazone Hydrochloride, and Their Selective Assay. K. Soda, T. Yorifuji, H. Misono and M. Moriguchi. *Biochem. J.,* **114**, 629 (1969).—A spectrophotometric method with 3-methyl-2-benzothiazolone hydrazone hydrochloride was developed for the determination of pyridoxal and pyridoxal 5′-phosphate, and for the selective determination of each in the presence of the other. Pyridoxal and pyridoxal 5′-phosphate react with the reagent to yield the azine derivatives, which give characteristic absorption spectra. The highest extinction values are obtained when pyridoxal and pyridoxal 5′-phosphate are incubated at pH values of about 3.4 and 8.0 respectively; their maxima are at 430 nm. (ε 2.74×10^4) and 380 nm. (ε 2.24×10^4) respectively. The azine of pyridoxal is only slightly soluble under the neutral and alkaline conditions, whereas that of pyridoxal 5′-phosphate is substantially insoluble in the acid pH range. This difference in solubility of the azines made possible the selective determination of pyridoxal and pyridoxal 5′- phosphate. *α*-Oxoglutarate and pyruvate are among the substances shown not to interfere with the assay of pyridoxal; their derivatives absorb appreciably only at wavelengths below 420 nm. For the assay of pyridoxal 5′-phosphate in the presence of these compounds measurement at 390 nm. is necessary.

Characterization of RNA Transcribed *in vitro* on Phage *ϕ*80 DNA. T. Okamoto, M. Sugiura and M. Takanami. *Biochem.*, **9**, 3533 (1970).—The characterization of the RNA species transcribed *in vitro* on phage *ϕ*80 DNA by *E. coli* RNA polymerase was based on the finding that the RNA chains were initiated with purine nucleoside triphosphates. It was demonstrated that four different sizes of RNA with unique starting sequences were transcribed on the tempelate. With enzyme lacking the *σ*-factor, the starting sequences and size became heterogeneous. The results indicate that the *ϕ*80 DNA molecule provides four sets of specific initiation and termination sites for *E. coli* RNA polymerase.

RNA Polymerase *σ*-Factor and the Selection of Initiation Site. M. Sugiura, T. Okamoto and M. Takanami. *Nature,* **225**, 598 (1970).—RNA polymerase lacking *σ*-factor can transcribe the replicative form of phage fd DNA quite well, but

loses the ability to select the appropriate initiation sites on the template, and both strands are transcribed. When σ-factor is added, the specificity and asymmetry of transcription are restored. The σ-factor restricts initiation to specific sites on the DNA template.